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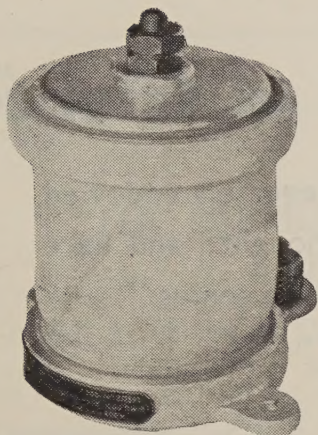
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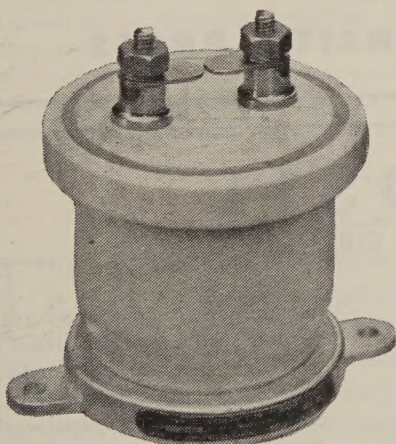
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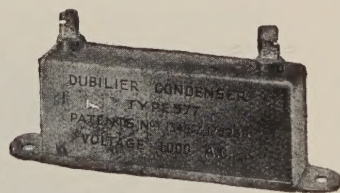
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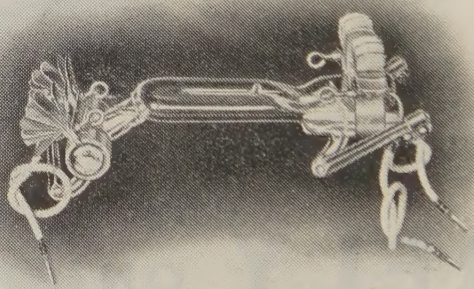
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THE DIFFRACTION OF X-RAYS BY LIQUID SULPHUR

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Reading University

Communicated by Prof. J. A. Crowther, November 5, 1932. Read April 7, 1933

ABSTRACT. The X-ray diffraction effects given by liquid sulphur at various temperatures between 130° and 260° C. are measured. The results indicate that the diffraction is caused by an unstable grouping of atoms of sulphur; the grouping becomes less pronounced with increased temperature, and changes in form gradually up to 220° C., when there is a sudden alteration corresponding to the change from the form S_{λ} to S_{μ} . Raman and Ramanathan's theory of X-ray scattering by liquids is found to be applicable to some extent at temperatures near the melting-point.

§ 1. INTRODUCTION

THE investigation described in this paper was undertaken to determine, as far as possible, the structure of sulphur in the liquid state from a temperature of 130° C. to 260° C., this range including the transition stage from the light yellow mobile liquid formed just above the melting-point to the dark brown viscous liquid formed near 200° C. The X-ray diffraction effects were obtained photographically and measured photometrically.

§ 2. EXPERIMENTAL DETAILS

The source of radiation was a Shearer tube, fitted with a molybdenum anticathode. The tube was operated by a 2-kilowatt transformer and took a current of 5–6 mA. at 75,000 V. The rays emerged through an aluminium window 0.05 mm. in thickness, and the beam was cut down by a lead stop 0.2 cm. in diameter before passing into the camera. The camera consisted essentially of a collimator, a cell containing the sulphur, and a film holder. The collimator was made of brass tubing 5 cm. long, fitted at each end with lead discs, bored centrally with holes of diameter 0.15 cm. The cell was made of aluminium foil, 0.01 mm. in thickness, and distance pieces were

arranged in it so that the collimated beam of X-rays transversed a thickness of 0.3 mm. of sulphur. The cell and sulphur could be heated electrically to any required temperature, which was measured by a platinum-platinum-iridium thermocouple. The beam of X-rays traversing the sulphur was diffracted, the diffraction haloes being then recorded on a Kodak Duplitzed X-ray film.

The production of each photograph was made under as nearly constant conditions as possible, by giving an exposure of $3\frac{1}{2}$ hours at 5 mA. and developing and fixing with solutions of the same strength for equal times. To prevent fogging of the film the central beam was absorbed with a lead disc placed near the film for the main part of the exposure, the lead disc being removed for a few minutes at the end of the exposure in order to record the position of the centre of the halo.

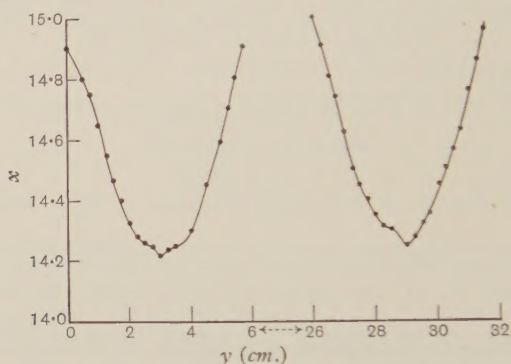


Figure 1.

The photometer for measuring the diameters of the diffraction haloes consisted of a 25 candle-power lamp fitted with a thin cylindrically coiled filament, the light from which was focused on the film under measurement. The light was passed through a water cell to prevent undue heating of the photographic film, and suitable stops prevented any light, excepting a good image of the filament, from falling on the film. A measure of the intensity of light emerging from the film was given by the current produced in a vacuum photoelectric cell. The film was held between two brass plates, which could be traversed by a screw in a plane perpendicular to the incident light, and the position of the film in the holder was adjusted so that observations could be taken for various positions of the filament-image on a diameter of the halo. The deflection x of the galvanometer in the photoelectric cell circuit was plotted against the distance of traverse y of the film, the positions of the diffraction peaks being then shown as minima. Figure 1 shows the type of curve obtained for sulphur just above the melting-point.

The diffraction effects caused by the aluminium cell were first recorded and then photographs were taken for sulphur at temperatures of 130° , 155° , 182° , 221° , 225° and 260° C. By suitable adjustment of the current in the heating coil these temperatures were maintained within 2° C. Each halo was measured along three or four diameters and the probable error of the diameter was computed. The liquid sulphur in the cell was replaced by finely crushed solid sulphur and the diffraction effects were

photographed for comparison. Finally, the cell was filled with finely crushed sodium chloride to determine, from the diffraction, the distance p from the cell to the photographic plate in the camera.

p

Well-marked diffraction haloes were obtained just above the melting-point, the haloes becoming more diffuse and fainter as the temperature increased. This increased the difficulty of estimating the positions of the diffraction peaks with increase of temperature, producing a decrease in the accuracy of measurement of the diameters of the haloes. From Bragg's law of diffraction, the diffraction haloes may be taken to indicate an effective periodicity d of electron-density-distribution in planes, and in all directions in the liquid, given by

d

$$\lambda = 2d \sin \theta,$$

where θ is the glancing angle for the given distribution of electrons, $\tan 2\theta$ being then given by r/p , where r is the radius of the halo and p , measured as above, is 6.40 cm.

θ

r

Both the diffraction rings given by crushed salt and solid sulphur showed that only the $K\alpha$ radiation of molybdenum was recorded on the photographs. Hence d was calculated from the equation:

$$0.712 = 2d \sin \left(\frac{1}{2} \arctan \frac{r}{p} \right).$$

§ 3. THEORIES

There are two main theories of X-ray diffraction in liquids to which the results obtained in the present investigation may be applied. The theory of Stewart postulates that in certain organic liquids the molecular forces and shapes are such that an entirely random distribution is not produced, and, in fact, that unstable groupings are produced throughout the liquid, and that in such groups there are recurring planes of maximum density of distribution of electrons. The quantity d , found above, then refers to the distance of separation of such planes.

On the other hand, the theory of Raman and Ramanathan shows that, if the molecules are assumed to be symmetrical, there will be a maximum diffraction of X-rays at an angle given by Bragg's equation $\lambda = 2d \sin \theta$, where d is the average distance of separation of the molecules. The results will, therefore, be applied to see if d can be more favourably interpreted as an inter-planar distance, or an average distance of separation of scattering centres.

A third way in which diffraction in liquids has been treated is based on the Ehrenfest formula for the scattering of X-rays by electrons in pairs, at a distance s apart. On this theory the mean distance between scattering centres, assumed to be atoms or molecules, is given by

s

$$s = 7.72 / (4\pi \lambda^{-1} \sin \theta) = 1.23d.$$

The mean distance d_0 of separation of the atoms of sulphur may be calculated, the closest packing in spheres being assumed. It can be shown to be equal to $1.33 (M/\rho)^{\frac{1}{3}}$ Å., where M is the atomic weight of sulphur on the hydrogen scale and ρ is its density.

d_0

M, ρ

d_1 Sulphur in the liquid state has a molecule containing 8 atoms, hence the average distance d_1 of separation of molecules is $2d_0$.

§ 4. RESULTS AND DISCUSSION

The results obtained are shown in table 1 and the values of d and d_0 are plotted in figure 2.

Table 1

$T(^{\circ}\text{C.})$	$r\text{ (cm.)}$	$d\text{ (\AA.)}$	$d_0\text{ (\AA.)}$	$S\text{ (\AA.)}$
130	$1.257 \pm .003$	$3.68 \pm .01$	3.47	$4.52 \pm .01$
155	$1.234 \pm .004$	$3.74 \pm .01$	3.48	$4.58 \pm .01$
182	$1.235 \pm .006$	$3.74 \pm .02$	3.49	$4.62 \pm .02$
221	$1.202 \pm .010$	$3.84 \pm .04$	3.49	$4.72 \pm .05$
225	$1.165 \pm .006$	$3.96 \pm .02$	3.51	$4.87 \pm .02$
260	$1.137 \pm .014$	$4.06 \pm .05$	3.52	$4.99 \pm .06$

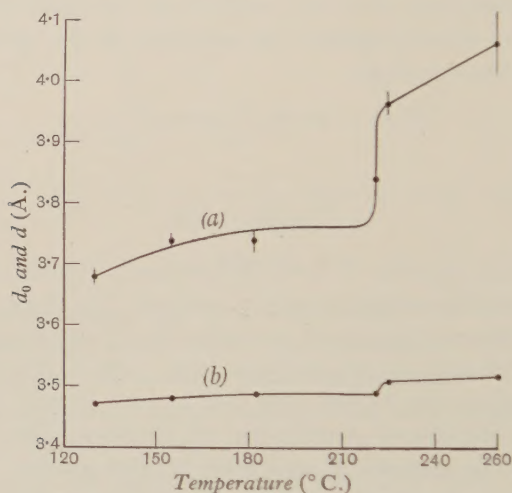


Figure 2. Values (a) of d and (b) of d_0 .

It is seen that there is a gradual increase of the distance d with temperature up to 220°C. , the rate of increase becoming less rapid as 220°C. is approached. At this temperature there is a sudden increase in d , which rises from approximately 3.79 \AA. at 220°C. to 3.95 \AA. at 223°C. There is thus a change of 4.2 per cent with 3°C. rise of temperature, after which d increases with temperature as before.

The photograph taken with crushed solid sulphur showed two main diffraction rings having radii of 1.40 cm. and 1.15 cm. There is thus a similarity between the solid and liquid diffraction; the halo produced at 130°C. , for example, has a radius which is close to the mean of the radii of the main diffraction rings for the solid. The flatness of the minima of the graphs also suggests the possibility of diffraction corresponding to more than one interplanar distance, but the photometer's resolving power was not sufficient to show such diffraction effects clearly, if present.

Sulphur crystallizes in the rhombic bipyramidal system, and work by W. H. Bragg* and Wigner and Mark† has shown that the crystal unit consists of 128 atoms of sulphur, arranged as 16 interpenetrating lattices of the rhombic bipyramidal element, having a equal to 10.61, b to 12.87, and c to 24.56 and containing 8 atoms of sulphur arranged as shown in figure 3. The rings obtained for solid sulphur correspond to diffraction by the (040) and (222) planes, the glancing angles obtained experimentally being $6^{\circ} 10'$ and $5^{\circ} 6'$. The mean value $5^{\circ} 33'$ of θ obtained for sulphur at 130°C. , and the distinct possibility that it may be an average value for two maximum diffraction angles (see figure 1), strongly suggest that the forces determining the crystal structure of sulphur are still effective to a marked degree in the liquid structure just above the melting-point, and that grouping of the atoms to form an unstable lattice occurs. Further, the liquid diffraction at 130°C. , although it is more diffuse than that of the solid sulphur, is intense, showing that the grouping of atoms is a general and well-marked feature of the structure at temperatures just above the melting-point. The effect of temperature will now be considered.

If the measurement d is an interplanar distance, or an average distance of separation of molecules, it is to be expected that it will show some relation to the expansion of sulphur. The volume of 1 gm. of sulphur at various temperatures in the range under consideration is plotted in figure 4 from data from the *International Critical Tables*. There is seen to be a discontinuity in curve (a) of figure 2, and a corresponding discontinuity must also be assumed from the points plotted in figure 4.

Numerical comparisons may be made as follows:

From 134°C. to 210°C.

Figure 2 (a). Concave downwards with an increase in d of 2.3 per cent.

Figure 4. Concave downwards with an increase in $1/\rho$ of 1.9 per cent.

Near 220°C.

Figure 2 (a). A sudden increase in d of 4.1 per cent.

Figure 4. A sudden increase in $1/\rho$ of 0.7 per cent.

From 225°C. to 260°C.

Figure 2 (a). An increase in d of 2.5 per cent.

Figure 4. An increase in $1/\rho$ of 1.3 per cent.

If the diffraction in the liquid is caused by an unstable modification of the crystal structure, and corresponds to diffraction by the (040) and (222) planes in the crystal, the percentage increase in d denotes the percentage increase in the dimensions of OB and OP where P is the foot of the perpendicular to the (222) plane ABC , figure 3. It may reasonably be assumed that increased kinetic energy of the sulphur atoms tends to produce a more random distribution, gradually obliterating the effect of forces tending to produce regular grouping of the atoms, and therefore that as the temperature is increased, the atoms still group in roughly the same form, but the lattice is modified so that the various interplanar distances become more nearly

* *Proc. R. S. A.*, **89**, 575 (1914).

† *Z. Phys. Chem.*, **111**, 398 (1924).

equal. This might come about, for example, by the atoms in the planes $OAFB$ and $DCEG$ moving further apart on the average, and the distance of separation DB of such planes being reduced. The photographs give evidence of the distance corresponding to OB increasing, but the distance DB is not shown by the diffraction effect in the liquid.

Applying this theory to the results obtained it is seen that there is an increase in OB of approximately 2.3 per cent from 134° to 210° C., and from the symmetry of atoms in the plane $OABF$ it may be assumed that there is an increase in the direction OA of about the same magnitude. This is equivalent to assuming that atoms in (001) planes, e.g. O and A , will be displaced from an atom K in approximately the same proportion with increased temperature. Now there is an increase of $1/\rho$ equal to 1.9 per cent, and therefore an average decrease in DB of $(4.6 - 1.9)$ or 2.7 per cent

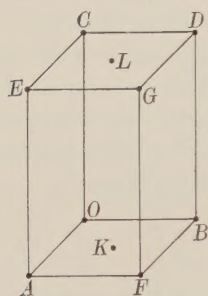


Figure 3.

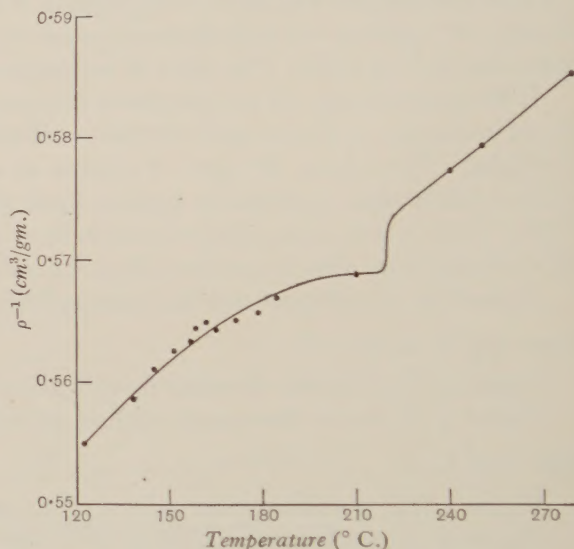


Figure 4.

will be required to explain this result. Thus it seems feasible that as the temperature rises the unstable lattice of sulphur gradually expands along OA and OB and contracts along OC . The photographs indicate that at somewhere near 220° C. there is a comparatively sudden change in d , which must mean that the increased kinetic energy of the atoms of sulphur makes possible a new unstable lattice. Thus, on the assumptions made before, there will be something in the nature of a fairly sudden increase with temperature in OA and OB of 4.1 per cent each, and the increase of 0.7 per cent in $1/\rho$ requires a decrease in OC of $(8.2 - 0.7)$ or 7.5 per cent. The effect of increase of temperature from 130° C. to 220° C. is repeated above 220° C. in a more marked manner, there being an increase in OA and OB of 2.5 per cent and a decrease in OC of $(5.0 - 1.3)$ or 3.7 per cent.

In figure 5 d is plotted against $\rho^{-\frac{1}{3}}$. If the diffraction effects were simply due to a random orientation of atoms or molecules d would be directly proportional to $\rho^{-\frac{1}{3}}$.

Experimentally a curve is found with a distinct break indicating the change in structure near 220°C .

The effect of change of temperature on the diffraction of X-rays by organic liquids has been investigated by Skinner, who found increases with temperature in the planar distances occurring in unstable groups of molecules, which were, in some cases, three times the coefficient of expansion, and actual decreases of interplanar distances with increase of temperature were also measured. The above discussion points to similar effects occurring in an unstable lattice of atoms of sulphur in the liquid state.

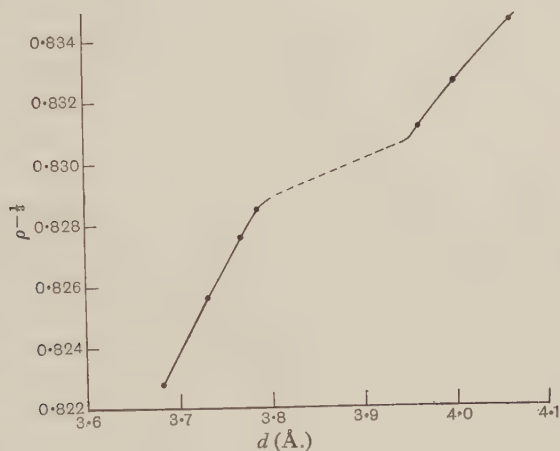


Figure 5.

Applying the results to the theory of Raman and Ramanathan we see from table 1 that the mean distance d_1 of separation of molecules of sulphur at 130°C . = $2d_0 = 6.94\text{Å}$., a value which is hopelessly out of agreement with the value 3.68Å . found by experiment at this temperature. The diffraction, therefore, does not appear to be due to random molecular distribution. If, however, the average distances of separation of the sulphur atoms are examined, more definite conclusions can be reached; d_0 and T are plotted at (b) in figure 2, and it is seen that the value of d_0 is about 6 per cent lower than that of d at 130°C ., and that as the temperature increases the values of d and d_0 diverge slightly from one another, d being about 12 per cent greater than d_0 at 260°C . If the theory of Raman and Ramanathan were accurately true d would be equal to d_0 at all temperatures, and from the present experiments it may therefore be concluded that the theory is more nearly true for the case of sulphur near the melting-point. It is seen, however, that the large jump in the value of d near 220°C . cannot be accounted for on Raman and Ramanathan's theory, and the rough agreement found therefore seems to be arbitrary. Also, from the magnitude of d by experiment, and d_0 by calculation, it is again evident that the diffraction is related to interatomic distances, and not to intermolecular distances as in the case of organic liquids*.

* *Phys. Rev.* 30, 232 (1927); 31, 20 (1928); 32, 153 (1928).

Considering now the theory based on the Ehrenfest formula, if the scattering centres are taken as being molecules S should have the value 6.94 \AA. at 130° C. as previously calculated, whereas it is found by experiment to be 4.52 \AA. Here, as with Raman and Ramanathan's theory, the facts fit the theory better if the scattering centres are taken to be single atoms. Even then the value 4.52 \AA. of S is about 25 per cent higher than the value 3.47 \AA. of d_0 . Also from table 1 it is seen that the value of S increases more rapidly with temperature than that of d_0 . The experiments, therefore, indicate that the Ehrenfest formula is inapplicable to the liquid state, and that the theory of Raman and Ramanathan is more applicable near the melting-point, the scattering centres in the case of sulphur being single atoms. The theory of unstable grouping gives most satisfactorily the structure of liquid sulphur just above the melting-point and the type of changes which may be expected to occur for a range of temperature from 130° to 260° C.

The results fit in well with the chemical facts and the theory which has been deduced. The generally accepted theory, proposed by A. Smith and W. B. Holmes*, is that there are two forms of sulphur, the one soluble in carbon bisulphide, designated S_λ , and the other insoluble, designated S_μ . A small proportion of S_μ is formed as soon as the sulphur melts, and the amount increases as the temperature rises according to the reversible reaction $S_\lambda \rightleftharpoons S_\mu$. At 160° C. the sulphur is a saturated solution of S_μ in S_λ containing about 12 per cent of S_μ , and above 160° C. supersaturation of S_μ in S_λ occurs, and a second phase appears consisting of a solution of S_λ in S_μ , the proportion of S_λ decreasing as the temperature increases. The presence or absence of foreign matter in small quantities affects to a considerable extent the temperature of greatest viscosity. Further, it has been shown by Trillat† that if the structure of viscous sulphur is stabilized by quenching in water, exposure to X-rays greatly accelerates the change to the ordinary soluble form. Hence the action of X-rays in the reversible reaction $S_\lambda \rightleftharpoons S_\mu$ is to favour the formation of S_λ , thus producing the transition point at a higher temperature in the present experiments. The fact that transition from S_λ to S_μ occurs at 220° C. instead of near 160° C. is therefore readily explained. This leads to the conclusion that S_λ is the form of sulphur in which the atomic forces produce unstable grouping, as described above, and that S_μ is a form of sulphur in which the unstable grouping is changed in the manner previously suggested. The increased viscosity of S_μ form may, in this case, be caused by the increased interpenetration of the rhombic bipyramidal elements containing 8 atoms, which would be expected to produce a more cohesive liquid.

§ 5. ACKNOWLEDGMENT

In conclusion the author wishes to thank Prof. J. A. Crowther for suggesting the problem discussed in this paper, and for the helpful interest he has shown during the course of the work.

* J. W. Mellor, *Theoretical Chemistry*, 10, 46 (1927).

† *Comptes Rendus*, 192, 559-61 (1931).

THE HYPERFINE STRUCTURE OF PERTURBED SERIES

By E. GWYNNE JONES, Beit Scientific Research Fellow,
Imperial College, London

Communicated by Prof. A. Fowler, F.R.S., February 2, 1933. Read April 7, 1933

ABSTRACT. A discussion of the hyperfine structures of the terms in perturbed series is given, and rules governing such effects are derived. It is found that these rules are not analogous to those obtained from the analysis of multiplet structures.

§ 1. INTRODUCTION

FROM a discussion* of term series which do not obey the usual Ritz formula it has been shown that when an atom has states of nearly equivalent energy arising from different electron configurations these states may suffer mutual perturbation. Experimentally the perturbations are recognized as apparent "repulsions" between terms having the same L and J values. From their analysis Shenstone and Russell were able to represent a series, perturbed by a foreign term ν_0 of the same type, by the formula

$$\nu_n = R/(n + \delta)^2; \quad \delta = (\mu + \alpha\nu_n + \beta/\nu_n - \nu_0) \dots\dots(1),$$

where R , n , μ and α are the usual constants of the Ritz formula and the expression $\beta/(\nu_n - \nu_0)$ is due to the perturbing effect. It appears that the constant β , which governs the magnitude of the perturbation, is essentially the same for all the members of mutually perturbing multiplets (cf. the $^3D_{1,2}$ and 3 of Ca I, for which $\beta_1 = -85$; $\beta_2 = -86$ and $\beta_3 = -90$). On the other hand, β appears to be slightly different for the various isotopes of a given element. Later it was found† that when terms of different types lie so near together that their mutual separation is comparable with their hyperfine separations, perturbations may occur between hyperfine levels having the same quantum numbers. In the following discussion it will be shown that an extension of the above viewpoints affords an explanation of several anomalies in the results of hyperfine-structure investigations.

§ 2. THE HYPERFINE STRUCTURE OF THE $6s.mp.^1P_1$ SERIES OF Hg I

The analysis‡ of the hyperfine structures occurring in the mercury spectrum shows that the terms of the two odd isotopes, 199 and 201, possess hyperfine structures arising from the interaction of nuclear magnetic moments, I_{199} equal to $\frac{1}{2}$ and

* A. G. Shenstone and H. N. Russell, *Phys. Rev.* **39**, 415 (1932).

† H. Schüller and E. G. Jones, *Z. f. Phys.* **77**, 801 (1932).

‡ H. Schüller and J. E. Keyston, *Z. f. Phys.* **72**, 423 (1931); H. Schüller and E. G. Jones, *Z. f. Phys.* **74**, 631 (1932).

I_{201} equal to $\frac{3}{2}$, with the total moment J of the external electrons of the atom, and that the terms of the even isotopes—only 198, 200, 202 and 204 come into question for spectroscopy—are single, indicating the absence of nuclear magnetic moments. The hyperfine structure of the term 6^1P_1 is shown diagrammatically in figure 1, from which it is seen that the levels of the odd isotopes are grouped regularly about the unresolved terms of the even isotopes, together with which the optical "centres of gravity" of the levels of the odd isotopes fall. Important features of the mercury hyperfine structures are that (a) the levels of Hg^{201} are always inverted with respect to those of Hg^{199} , cf. figure 1; and (b) in terms characterized by $J = 1$ the total hyperfine separations for the odd isotopes are, in the absence of disturbing influences, the same*. In some terms, generally those associated with s -electrons, a further complication enters, whereby the levels of the several even isotopes (although individually not split, as no nuclear magnetic moments are present) are separated, in the order of their mass-numbers, by the operation of the isotopic displacement effect.

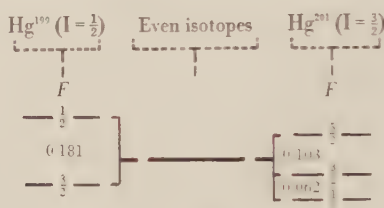


Figure 1. The hyperfine structure of the level 6^1P_1 of Hg I .

In the $6s.mp^1P_1$ sequence of Hg I , the lowest member, 6^1P_1 , has hyperfine structure separations $\Delta\nu \approx 0.175 \text{ cm}^{-1}$ for the odd isotopes and the levels of the even isotopes are coincident; this measured structure is in agreement with the structures of the other members of the $6s.6p$ multiplet. It would be expected, both on experimental and theoretical grounds, that the higher 1P_1 terms should possess structures and isotopic displacements smaller than those of the lowest term. The 8^1P_1 , which is, however, perturbed† by the presence of $d^9.s^2.6p.^1P_1$ some 1100 cm^{-1} lower in the energy diagram, shows an anomalous increase in hyperfine separation to $\Delta\nu = 0.385 \text{ cm}^{-1}$ and in isotopic displacement to 0.060 cm^{-1} ; the hypothetical unperturbed 8^1P_1 should have equal separations not greater than 0.175 cm^{-1} for both odd isotopes, see figure 2. Considering first the perturbation in Hg^{199} and remembering that a perturbation is apparent as a repulsion of terms with the same quantum numbers, it is clear that the observed increase in the hyperfine separation can only occur if the mutual perturbation of the $(F = \frac{1}{2})$ levels is greater than that of the $(F = \frac{3}{2})$ levels, i.e. $\Delta_{\frac{1}{2}} > \Delta_{\frac{3}{2}}$, and, as the other quantities in equation (1) are the same for all the hyperfine levels concerned, $\Delta \propto \beta$, whence, setting $\beta = \beta_{(J)} + \beta_{(F)}$ so that $\beta_{(J)}$ shall be the perturbation constant for the centre of gravity of the level and $\beta_{(F)}$ shall measure the second-order differential effect, we find that

$$\beta_{(F)}^{199} > \beta_{(F+1)}^{199} \dots [I = \frac{1}{2}; \quad g(I) > 0] \quad \dots (2).$$

* Schüler and Jones, *loc. cit.*

† Shenstone and Russell, *loc. cit.*

Similarly, for Hg^{201} , the mutual perturbation of the ($F = \frac{5}{2}$) levels must be greatest and that of the ($F = \frac{1}{2}$) levels least, thus,

$$\beta_{(F)}^{201} < \beta_{(F+1)}^{201} \dots [I = \frac{3}{2}; \quad g(I) < 0] \dots (3).$$

Also the various levels are so perturbed that the Landé interval rule, necessarily obeyed by the unperturbed term, holds for 8^1P_1 after the perturbation.

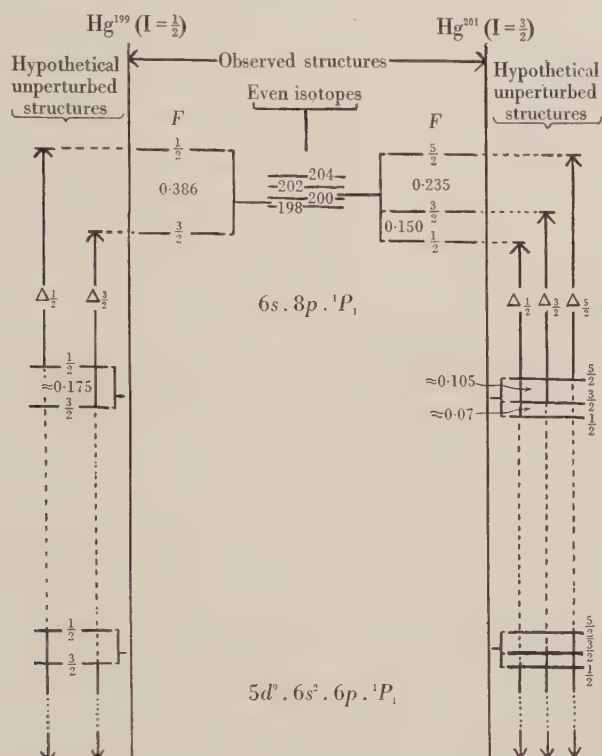


Figure 2. The perturbation of the hyperfine structure of 8^1P_1 of HgI.

The appearance of an isotopic displacement in 8^1P_1 , see figure 2, indicates that the perturbation constant β is different for the nuclei of different isotopes and, because the term of Hg^{204} lies highest in the diagram when the perturbation is from below,

$$\beta^{204} > \beta^{202} > \beta^{201} > \beta^{200} > \beta^{199} > \beta^{198} \dots (4),$$

where the constants for the odd isotopes refer to the perturbation of the respective optical centres of gravity.

The hyperfine structure of the unperturbed $d^9.s^2.p.^1P_1$ cannot be estimated, as this term is influenced by the whole of the 1P_1 series in the midst of which it lies.

§3. THE HYPERFINE STRUCTURES OF THE 2D -TERMS OF Pb II

Two sets of 2D -terms, arising respectively from the configurations $6s^2.md$ and $6s.6p^2$, have been recognized in the Pb II spectrum. The four lowest members, all of which have been investigated* for hyperfine structure, are unusual in that the $6s^2.6d$ doublet lies entirely within that of the $6s.6p^2$ configuration; see figure 3.

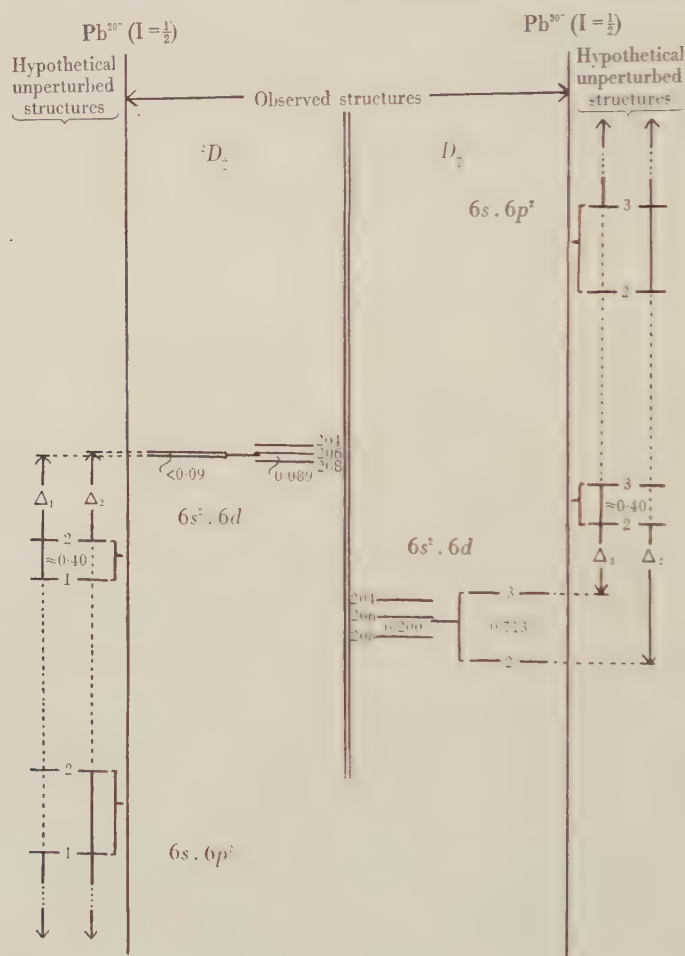


Figure 3. The perturbation of the hyperfine structures of the $6s^2.6d.^2D$ terms of Pb II.

The separation of terms with similar J -values is such that selective perturbations of their structures might be expected to occur.

The analysis of the hyperfine structures in the lead spectra indicates that the

* H. Kopfermann, *Z. f. Phys.* **75**, 363 (1932); H. Schüler and E. G. Jones, *Z. f. Phys.* **75**, 563 (1932); J. Rose and L. Granath, *Phys. Rev.* **40**, 760 (1932).

even isotopes 208, 206 and 204 have zero nuclear magnetic moments, and that all the resolvable terms of Pb^{207} are double; whence $I_{207} = \frac{1}{2}$.

The presence of a perturbation is evident from the abnormalities of the $6s^2.6d$ terms in respect to both coarse and hyperfine structure—the doublet is inverted and the hyperfine separations and isotopic displacements of $^2D_{\frac{3}{2}}$ are much larger than those of $^2D_{\frac{5}{2}}$. If any difference were expected between these terms, it would be that the hyperfine separation should be slightly larger for $^2D_{\frac{3}{2}}$. The perturbation which causes these anomalies is represented in figure 3. As $6d.^2D_{\frac{3}{2}}$ is perturbed from below and $6d.^2D_{\frac{5}{2}}$ from above, it is clear that their structures will be influenced in opposite senses; the fact that the structure of the former has been decreased and that of the latter increased leads to the result that the perturbation constant is greater for the hyperfine level of the smallest F value, or

$$\beta_{(F)}^{207} > \beta_{(F+1)}^{207} \dots [I = \frac{1}{2}; \quad g(I) > 0] \quad \dots(5).$$

The observed perturbation of the isotopic displacements again requires, as for Hg, that the perturbation constant be greatest for the heaviest isotope:

$$\beta^{208} > \beta^{207} > \beta^{206} > \beta^{204} \dots \quad \dots(6).$$

If it be assumed that the magnitude of the perturbation of the isotopic displacements is approximately the same for both sets of terms, then the unperturbed displacement effect of the $6d$ electron will be about 0.14 cm^{-1} . In Pb I, terms involving a $6d$ electron have isotopic displacements of approximately 0.030 cm^{-1} , which is equivalent to an effect of about 0.12 cm^{-1} in the first spark spectrum. This agreement in order of magnitude also supports the view that the two sets of 2D -terms suffer mutual perturbations.

§ 4. OTHER SERIES WITH PERTURBED HYPERFINE STRUCTURES

Many series in the spectra of other elements show the characteristic perturbations described above. The lowest terms of the $3s.mf.F$ series in Al II, which are strongly perturbed by terms of the $3p.3d$ configuration*, all possess a doublet structure, which, in view of the above discussion, may be regarded as a greatly perturbed hyperfine structure†. In the arc spectrum of lead the p^3P_1 series show slight perturbations in their hyperfine structures; owing to the fact that each term is perturbed by the whole s^3P_1 series the net effect is therefore small and no isotopic displacements are produced. The hyperfine structures of Tl II also show the presence of many small perturbations in the higher members.

§ 5. DISCUSSION

The above examples show conclusively that the rules obtained for the mutual perturbations of hyperfine structure levels are not what would be expected from a consideration of analogous perturbations in the coarse-structure terms. Hyperfine levels, of given J and I , have perturbation constants $\beta_{(F)}$ which show a complicated

* Shenstone and Russell, *loc. cit.*

† This would indicate that Al^{27} has a nuclear moment I equal to $\frac{1}{2}$.

dependence upon their F values, whilst coarse-structure levels, of given L and S , have the same perturbation constant which is independent of their J values. This result is very surprising, for it has always been possible to derive rules applicable to hyperfine structures by the substitution of J , I and F for the quantum numbers L , S and J , respectively, in the corresponding rules for coarse structures. In particular, the usual intensity and interval rules, in their modified form, are strictly valid in hyperfine structures.

The selective perturbations found in mercury show unambiguously that the nature of the effect is governed by the sign of the $g(I)$ factor—the ratio of the magnetic to mechanical moments—of the nucleus concerned. The perturbations in Hg^{199} and Pb^{207} are particularly interesting as both atoms have the same nuclear moments and similar $g(I)$ factors: the same variation of $\beta_{(F)}$ is obtained in both cases, whether the hyperfine levels are normal (Pb^{207} , figure 3) or inverted (Hg^{199} , figure 2).

The differential perturbation of the terms of the individual isotopes is also independent of their relative energies, for in lead the isotopic displacements are inverted with respect to those in mercury; nevertheless the terms of the heaviest isotopes suffer the greatest perturbation in both elements. It is evident that this regular increase of the perturbation constant with the mass number is a fundamental property of the nucleus and is unaffected by the external electronic structure which causes the inversion of the isotopic displacements in the transition from mercury (normal state $6s^2$) to lead ($6s^2.6p^2$). It would seem that the perturbation of the individual terms is due to a mutual sharing of identities by two valency electrons on account of their electrical interaction; for a given element this interaction might be affected by a change in some electrical property (e.g. the polarizability) of the nucleus from one isotope to the next, which would produce the observed slight differences in the perturbation constants. If the nuclei of the various isotopes are considered to be built up from that of the lightest isotope by the addition of neutrons, a systematic change in the polarizability of the nuclei so formed would be expected.

With regard to the ultimate cause of the isotopic displacements, it is interesting to note that the effect occurs almost exclusively in terms associated with configurations containing two equivalent valency electrons. The effect is most marked in those spectra where the resonance energy of such equivalent electrons is small, i.e. where the intercombination lines are strong. If the electrical interaction responsible for the Heisenberg-Dirac resonance energy were affected by the polarizability of the nucleus, then the term values of the various isotopes would show all the characteristic features of the displacement effect.

548.712:549.514.1

QUARTZ AS A STANDARD FOR ACCURATE LATTICE-SPACING MEASUREMENTS

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ABSTRACT. A test has been made of the use of quartz as a standardizing substance for very accurate lattice-spacing determinations. With CuK_α radiation it gives a very good photograph with many sharp K_α doublets, which may be measured with accuracy. A redetermination of the axial ratio from an X-ray powder photograph gave

$$c/a = 1.10002 \pm 0.00004,$$

and this value was confirmed by X-ray measurements on several other crystals. Assuming Bergqvist's value for d_{100} (4246.02 X. units) we obtained $a = 4902.9$ X., $c = 5393.3$ X. Various specimens of quartz from different sources were compared by taking powder photographs in the same camera, one of the clear, colourless specimens being used to calibrate the camera, on the basis of the above values.

The values of d_{100} at 18° C. all lay between 4245.9₅ and 4246.30. The clear colourless crystals gave 4246.0 ± 0.05 .

§ 1. INTRODUCTION

ALTHOUGH the value of the lattice spacing of a crystalline substance is usually expressed in Ångstrom units, and a high degree of accuracy may often be claimed for the measurements, such values are not absolute but only relative. The value of the Ångstrom is based on optical measurements, whereas lattice-spacing values are derived from X-ray wave-lengths which have not yet been accurately standardized. The latter were originally obtained from measurements on rock-salt and calcite, for which the lattice spacings had been deduced from a knowledge of the density and molecular weight with the help of calculations involving Avogadro's number, which in its turn depends upon the experimental determination of e by Millikan*. Thus the whole scale of wave-length values is influenced by the accuracy of the determination of e , and since this has not yet been made with a high degree of accuracy it has been impossible from crystal measurements to obtain X-ray wave-lengths of great accuracy on an absolute scale.

Attempts have been made to eliminate this difficulty by using methods to

* *Proc. Nat. Acad. Sci.* 3, 314, (1917).

X.

determine X-ray wave-lengths which do not involve the use of the Avogadro constant. The usual method is that of the ruled grating*. Probably the most accurate measurements are those of Backlin† and Cork‡, which, however, give values different from those determined from crystal measurements by an amount which exceeds experimental error. It therefore seems probable that the scale of wave-lengths is in error owing to an inaccuracy in the value of e . On the other hand the direct measurements are themselves not yet sufficiently accurate to warrant a change in wave-length standards. It is therefore customary to use, as an arbitrary standard, Siegbahn's values expressed in X units (X.), of which the latest series is given in the second edition of *Spektroskopie der Röntgenstrahlen*§.

The object of our investigation was to find the most accurate means of basing powder-photographic determinations of lattice spacing on the Siegbahn scale of wave-lengths. In comparing the lattice spacing of a crystal with an X-ray wave-length, it is essential to measure the glancing angle of reflection. This may be found directly, but in X-ray powder photography greater accuracy is obtained if the instrument is first standardized by the use of a substance of known lattice spacing. The latter is either mixed with the material under investigation, or it may be used in a preliminary experiment in order to calibrate the instrument.

It is clearly an advantage to use for such a purpose a substance which has already been employed in the determination of wave-lengths by Siegbahn and his collaborators. Rock-salt was the first crystal to be used for wave-length measurements, but it has several serious disadvantages for powder photography, as well as for single-crystal measurements. It has been our experience that many samples of NaCl do not give sufficiently sharp reflections, and that there is a marked difference between the lattice spacings of different samples. This is in agreement with the work of Barth and Lunde¶, who have shown that the lattice spacing of chemically prepared NaCl is 5.626 Å., instead of 5.628 Å., which is the value universally assumed for natural rock-salt.

A suitable standard for use in X-ray powder photography must have a simple structure, and it should also have a low absorption coefficient for the radiation employed, in order to avoid the possibility of errors due to the displacement of lines by absorption. Of the substances other than rock-salt used in X-ray spectroscopy, we have found that calcite does not give very good photographs, probably on account of the high value of the primary extinction, and others, such as sugar and gypsum, give patterns that are much too complicated. After repeated trials we concluded that by far the best substance for the purpose was quartz. The present paper is an account of some experiments devised to test the suitability of quartz for the calibration of Debye-Scherrer cameras, where extreme accuracy might be desired.

* A. H. Compton and Doan, *Proc. Nat. Sci. U.S.A.* **11**, 598 (1925).

† *Dissert.* (Upsala, 1928); *Nature*, **125**, 239 (1930).

‡ *Phys. Rev.* **35**, 128 (1930).

§ Julius Springer, Berlin (1931).

¶ R. W. G. Wyckoff, *Z. Krist.* **59**, 55 (1923-4); Havighurst, Mack & Blake, *J. Amer. Chem. Soc.* **46**, 2368 (1924).

¶ *Zeit. f. Phys. Chem.* **126**, 417 (1927) also V. M. Goldschmidt, *G.V.* **8** (1927).

§ 2. DESCRIPTION OF CAMERA

In an earlier paper*, we have described a new method for the accurate determination of lattice spacings from Debye-Scherrer photographs. The film is placed round the circumference of the camera in the usual way (i.e. with the centre of the film corresponding to zero angle of reflection), but the ends of the exposed portion of the film are defined by means of two knife edges casting sharp shadows on the film†, as at *A*, *B* in figure 1*a*. The knife edges are close to the point *X* where the incident beam enters the camera, allowing reflections to strike the film up to very large angles. The angular ranges *YA* and *YB* correspond approximately to 165°. The limitation is imposed in order to allow the slit system to reach almost to the centre of the camera.

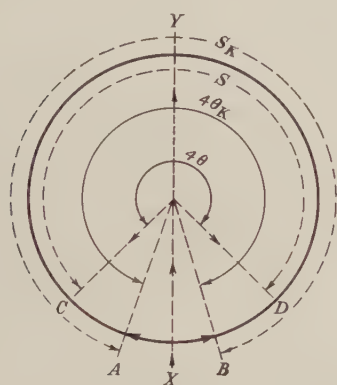


Figure 1*a*. Illustrating method of calibration.

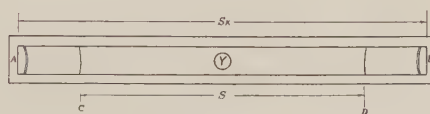


Figure 1*b*.

When the film is unrolled, it has the appearance of figure 1*b*, which is lettered to correspond with figure 1*a*. The distance between the two knife edges S_k corresponds to a definite angular range characteristic of the camera, θ_k . This is the only constant which has to be measured in order to calibrate the camera. However much the film shrinks,

$$\theta/\theta_k = S/S_k \quad \dots\dots(1),$$

where θ is the glancing angle of reflection corresponding to a distance S between the pair of lines in question. It is of course essential to measure S and S_k at the same time, as the film contracts and expands according to the state of the atmosphere.

It will be seen that the radius of the camera does not appear in equation (1). Also the lines at high angles, which give the spacing accurately, are in the neighbourhood of the standard shadow edges. The θ values from these lines are almost free from errors. The method has therefore all the advantages of the Van Arkel‡ arrangement

* *Proc. Phys. Soc.* **44**, 563 (1932).

† The use of knife edges for this purpose was adapted from the method employed by Phragmén in his precision camera. See A. Westgren, *Trans. Amer. Inst. Mining and Met. Eng.* **31**, 13 (1931).

‡ A. E. van Arkel, *Physica*, **6**, 64 (1926).

in which film-shrinkage errors at high angles are avoided by placing the film back to front (i.e. with the incident beam passing through the centre of the film).

The angle θ_k may be found from a direct measurement of the camera, but it is doubtful whether this gives an absolute accuracy of more than 1 part in 5000 in lattice spacing, since it is apt to introduce small errors which cannot be allowed for. For example, the shadows of the knife edges on the film may not coincide exactly with their calculated positions.

A much more accurate method of calibrating the camera is the use of a standard crystal, the spacings of which are accurately known. Errors in the camera constant are still introduced by this process of calibration, but they tend to cancel out when lattice spacings are being determined because every stage in the calibration process is repeated in the reverse direction. For example, no correction need be made for errors caused by the use of a beam of finite height, provided that this is the same in all experiments. Slight faults in the construction of the camera do not matter in this method.

Errors due to centring, absorption, and film shrinkage, which vary in amount from one photograph to another, require individual treatment. However, as we have shown, the ratio $S'S_k$ makes complete allowance for film shrinkage. The method of eliminating errors due to centring in the process of calibration is described later. With this method the camera constant may be obtained correct to about 1 part in 15,000, which is sufficient to give lattice spacings with an accuracy of about 1 part in 50,000 *relative to the chosen standard*.

§ 3. METHOD OF CALIBRATING CAMERA

The (100) spacing of quartz has been accurately determined by Bergqvist*, who used CuK radiation. The same radiation was employed in our experiments, so that there was no doubt about the accuracy of the (100) spacing d in terms of the wave-length.

Bergqvist gives:

$$\text{for } K\alpha_1, \lambda = 1537.395 \text{ X.}$$

$$\text{for } K\alpha_2, \lambda = 1541.232 \text{ X.}$$

$$\text{for quartz, } d = 4246.02 \text{ X. at } 18^\circ \text{ C.}$$

after correcting for the refractive index.

In Bergqvist's measurements the refractive index produced a considerable deviation from the simple law of X-ray reflection

$$n\lambda = 2d \sin \theta,$$

since he used the lowest orders of reflection. We worked only at high angles, where the effect was much less important, requiring only a small correction.

The c spacing of quartz was calculated from an assumed value of the axial ratio. Groth† gives $a : c = 1.0999$, as found by Kupfer‡ in 1825§. Combining this

* O. Bergqvist, *Z. f. Phys.* **66**, 494 (1930).

† *Chemische Kristallographie*, **1**, p. 86.

‡ *Preisschr. d. Akad. d. Wissensch.* **61** (Berlin, 1825).

§ A later determination by Tutton (*Crystallography*, p. 373) gives 1:1000.

with Bergqvist's value, we obtain for the axes $a = 4902.88$ X.; $c = 5392.68$ X. at 18° C.*

The c value cannot be exact, but it is accurate enough to fix the indices of the observed reflections. A very accurate determination of the axial ratio is made in the present paper, but at the beginning of the work the exact value was unknown.

The problem was to calibrate the camera, i.e. to find θ_k , without an accurate knowledge of c/a , and at the same time eliminate errors due to the centring of the specimen.

The use of a thin diluted specimen of quartz with CuK_α radiation eliminates absorption errors, but it is almost impossible to ensure that the specimen is exactly at the centre of the camera. This causes a systematic displacement of the lines on the film, which has a far greater effect at low than at high angles. In our former paper it was shown that accurate lattice-spacing determinations could be made by plotting the spacing values from individual lines against the corresponding values of $\cos^2 \theta$, and extrapolating a linear curve through the points to $\cos^2 \theta = 0$ †. This method must be slightly modified in order to determine θ_k , as the following considerations will show. From our earlier paper, the error dS in the measured distance between corresponding lines is given by:

$$ds = -2.p \cos \phi . \sin 2\theta \quad \text{.....(2)}$$

where p is the displacement of the specimen from the centre of the camera and ϕ is the direction of displacement measured from the direction of incidence. The error dS causes an error $d\theta_k$ in θ_k which is given by

$$\frac{d\theta_k}{\theta_k} = -\frac{dS}{S} = \frac{p \cos \phi}{R} \frac{\sin 2\theta}{2\theta} \quad \text{.....(3),}$$

R being the radius of the camera. .

Equation 3 shows that the value of $d\theta_k$ varies linearly with $\sin 2\theta/2\theta$, falling to zero when $\sin 2\theta/2\theta = 0$, and $\theta = 90^\circ$. If, therefore, the values of θ_k obtained from different lines be plotted against the corresponding values of $\sin 2\theta/2\theta$ a straight line should be obtained, and if this line be extrapolated to $\sin 2\theta/2\theta = 0$, the correct value of θ_k should be found, with a complete elimination of the errors caused by centring.

In practice the presence of individual errors of measurement prevents the values of θ_k from lying exactly on a straight line. They should, however, be grouped on either side of a straight line in a random manner if c and a are correct. If, however, an incorrect axial ration has been assumed, so that while a is correct c is in error, this will be shown by a systematic deviation of points corresponding to different sets of indices from a mean line. If, for example, the ratio c/a has been given too small a value, points for large values of l will fall above the mean line, the departure being greater the greater the value of l . A new value of the axial ratio

* W. Zachariasen, *Z. Krist.* **67**, 226 (1927), gives $a = 4.903$ Å., $c = 5.393$ Å., $c/a = 1.0999$.

† An extrapolation method was first used by Kettmann, *Z. f. Phys.* **53**, 198 (1929), who plotted the lattice-spacing values for individual lines against their θ values. However, since this curve turns over rapidly towards $\theta = 90^\circ$ it allows considerable latitude in the interpretation of the results.

must be found which brings all the points on to the same line, apart from random errors of measurement.

To sum up, the θ_k values found by applying equation (1) to each line on the film may be in error for two reasons. (i) The measured value of s may have systematic errors due to the eccentricity of the specimen in the camera. (ii) The calculated values of θ may have systematic errors due to inaccuracy of the axial ratio. These effects may be eliminated by the following procedure. (1) Plot the values of θ_k against the corresponding values of $\sin 2\theta/2\theta$. (2) Observe whether there is a systematic deviation of points about a mean straight line for planes with large and small values of l . Such an effect indicates an error in the axial ratio. (3) By a process of trial and error, find a value of the axial ratio which brings points for large and small values of l upon the same curve. (4) Estimate the camera constant θ_k by extrapolation to $\sin 2\theta/2\theta = 0$.

§4. LIMITS OF ACCURACY

The accuracy of the determination of θ_k depends upon the validity of the method for eliminating systematic errors, and on the accuracy of individual measurements. The former depends upon the absence of errors due to causes other than centring, while the latter depends on the intensity-distribution across the lines and on the measuring instrument.

In our experiments a camera of diameter 9 cm. was calibrated by means of a powder photograph taken with CuK_α radiation. β lines were eliminated by means of a nickel screen. The specimen was obtained by grinding up a crystal of pure quartz, which was mixed with about three times its own volume of Canada balsam and mounted on a hair at the centre of the camera, in the form of a cylinder 0.4 mm. in diameter. The displacement of the lines due to absorption of the Cu radiation by the specimen is almost eliminated by this procedure. Continual rotation of the specimen and a special slit system yield strong lines of symmetrical shape, with sharply defined peaks, which correspond closely to the centre of gravity of the lines.

A reproduction of one side of the quartz film is shown in figure 2*a*. Figure 2*b* shows an enlargement of the portion containing the resolved K_α doublets. Near the end of the film the doublets are sufficiently separated for the measurements to be uninfluenced by overlapping, and a very high accuracy can then be attained. To test the possible accuracy, photometer readings were obtained from the doublet for which $h\ k\ l = 2\ 3\ 4$. The microphotometer curve for this line is given in figure 3*a*, for which readings were taken at intervals of 0.01 cm. It is clear from this curve that the position of the peaks is not influenced by the presence of neighbouring lines.

An attempt was then made to find how accurately the position of the peak could be measured. The portions *AB*, *CD* at the summits of the curves, which were examined in detail, are reproduced in figure 3*b*. The readings were taken at intervals of 0.001 cm. It appears from these curves that the peaks may be measured to ± 0.0001 cm. This degree of accuracy is far beyond our requirements, and in practice measurements are made with a travelling microscope reading to 0.001 cm.

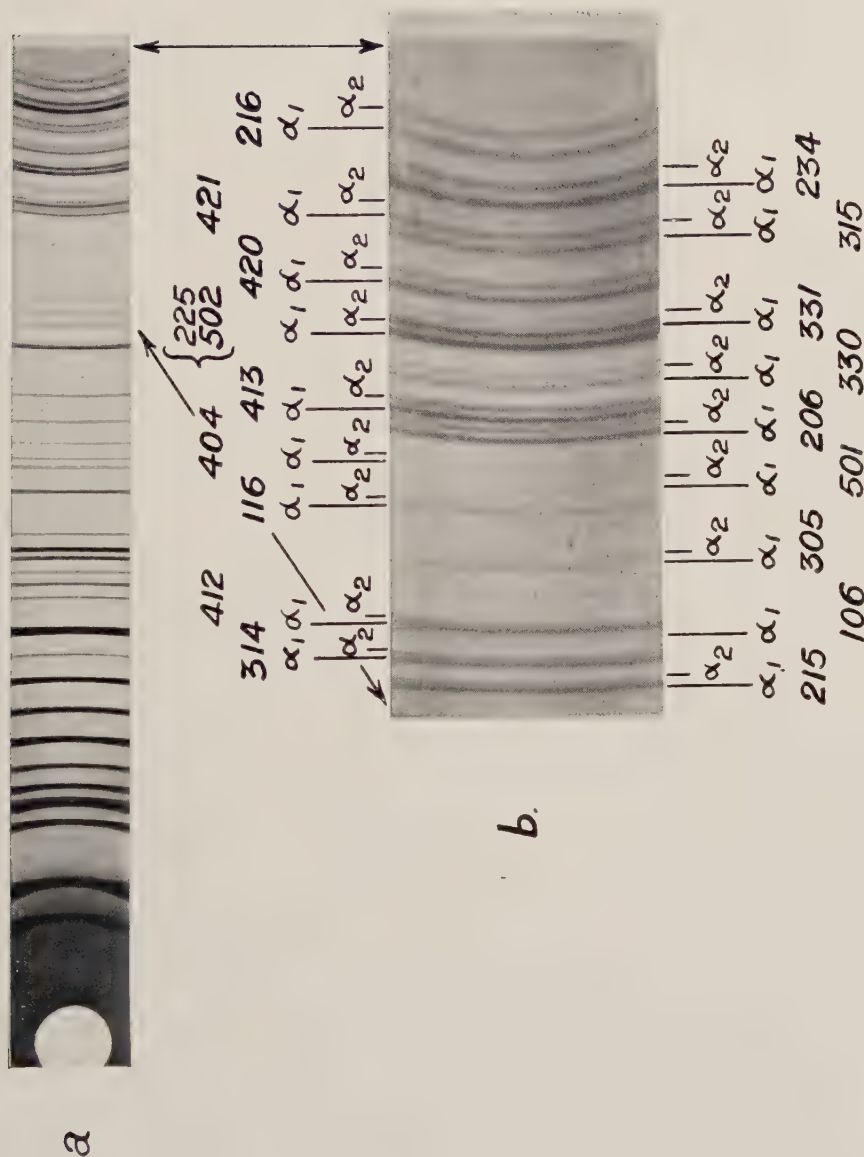


Figure 2. Powder photographs of quartz.

The limit of accuracy is then of the order of 0.001 cm. to 0.003 cm. for the distance between a pair of corresponding lines. This corresponds to an accuracy between about 1 part in 25,000 and 1 part in 10,000 in determining θ .

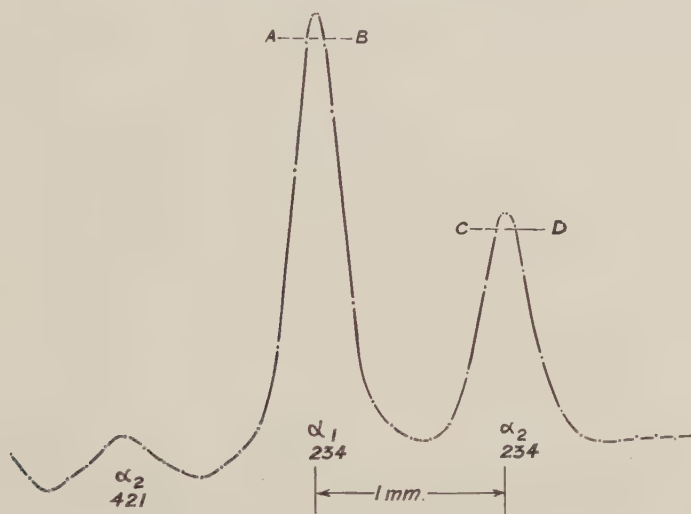
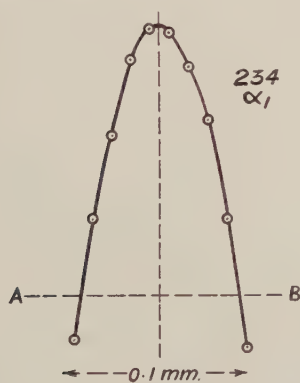


Figure 3a. Photometer curves of quartz.

(Mean bisector 0.9185 ± 0.0001 cm.)



(Mean bisector 0.8186 ± 0.0001 cm.)

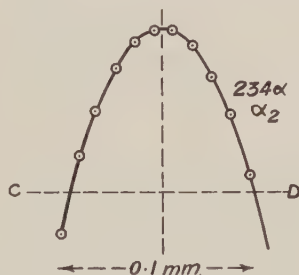


Figure 3b. \odot Photometer readings at intervals of 0.01 mm.

This high accuracy can only be attained in the case of strong lines near the end of the film where the doublets are well resolved. The other lines are less reliable and are only used as pointers, whereas the accurate lines serve as pivots for the extrapolation curve. It should be possible with one or two accurate doublets and a large number of pointers to obtain the value of θ_k to at least one part in 15,000.

Everything depends on the high angle lines. These must be close to the knife edges, and the film must be pressed down flat at this point. To ensure this, the ends of the film are slipped under a steel plate which holds them down firmly against the

circumference of the camera. It is not essential to avoid errors which influence only the lines at low angles. For example, if the film bulges slightly near the centre, both S and S_k are increased somewhat, but for the high angle measurements the ratio of S to S_k is scarcely affected. The measuring instrument need not be absolutely accurate along its whole length. It is sufficient if the small distances between S and S_k are measured accurately to 0.001 cm.

§ 5. RESULTS OF CALIBRATION AND REDETERMINATION OF AXIAL RATIO

Two series of calculated values of θ are given in table 1. Those on the left-hand side of the table are calculated for an axial ratio c/a equal to 1.0999 (Groth's value). Those on the right-hand side of the table are calculated for an axial ratio

Table 1. Calibration of camera 1

h, k, l	Radiation	Observed S (cm.)	Axial ratio $c/a = 1.0999$		Axial ratio $c/a = 1.10002$	
			θ^*	θ_k or $\theta S_k/S$	θ^*	θ_k or $\theta S_k/S$
412	α_1	19.556	61.313	82.906	61.312	82.905
	α_2	19.652	61.575	82.854	61.574	82.852
305	α_1	20.301	63.648	82.905	63.640	82.804
	α_2	20.395	63.938	82.899	63.930	82.888
116	α_1	20.937	65.636	82.898	65.624	82.882
	α_2	21.042	65.954	82.884	65.942	82.868
501	α_1	21.184	66.400	82.885	66.399	82.883
	α_2	21.288	66.729	82.888	66.720	82.888
404	α_1	21.432	67.175	82.882	67.169	82.874
	α_2	21.542	67.517	82.879	67.511	82.871
206	α_1	21.770	68.243	82.892	68.220	82.874
	α_2	21.885	68.603	82.892	68.590	82.874
413	α_1	22.007	68.965	82.867	68.961	82.862
	α_2	22.127	69.340	82.866	69.336	82.860
330	α_1	22.396	70.173	82.853	70.173	82.853
	α_2	22.527	70.573	82.841	70.573	82.841
502 } 225 }	α_1	22.868	71.650	82.851	71.646	82.847
	α_2	23.007	72.080	82.845	72.078	82.843
331	α_1	23.150	72.522	82.838	72.522	82.838
	α_2	23.150	72.522	82.838	72.522	82.838
440	α_1	23.407	73.332	82.843	73.332	82.843
	α_2	23.563	73.816	82.838	73.816	82.838
315	α_1	23.977	75.122	82.848	75.109	82.834
	α_2	24.138	75.629	82.851	75.622	82.843
421	α_1	24.310	76.154	82.836	76.154	82.836
	α_2	24.310	76.154	82.836	76.154	82.836
234	α_1	24.517	76.799	82.832	76.790	82.822
	α_2	24.719	77.423	82.823	77.413	82.812
216	α_1	25.088	78.600	82.845	78.576	82.820
	α_2	25.324	79.332	82.837	79.307	82.811
End of film:		26.443 (S_k)				

Extrapolated value for θ_k 82.77°, c/a being taken as 1.10002.

* Values of θ calculated from Bergqvist's d value with correction for refraction.

1.10002, which will be shown to be more nearly correct. For overlapping lines an estimated value depending on the relative intensities of the component parts is given for θ . The value of θ_k for each line was determined from θ , S , and S_k by means of equation (1); values for each line are shown in table 1.

A weighted mean was found for θ_k from each pair of K_α doublets by giving α_1 twice the weight of α_2 .

The presence of systematic errors was tested by plotting the values of θ_k from table 1 against $\sin 2\theta/2\theta$ in figure 4*a*. The values deduced, an axial ratio $c/a = 1.0999$ being assumed, are represented by crosses. The crosses show a gradual fall as $\sin 2\theta/2\theta$ falls, indicating that the specimen was incorrectly centred. However, they do not lie at random about a straight line but are distributed in a regular fashion.

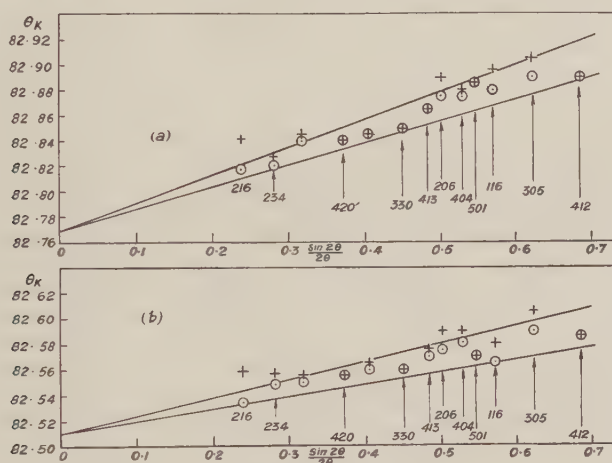


Figure 4.

Relatively higher values for θ_k are obtained from h, k, l planes with large values of l than from those with lower values of l . As we have shown, the effect may be explained by a small error in the assumed axial ratio. Planes with low values of l , being uninfluenced by the value of c , will tend to give a more correct value for θ_k than those with high values of l .

We have attempted to find a value of the axial ratio which would give no systematic variation in θ_k for high and low l indices. By trial and error the axial ratio 1.10002 was found to satisfy this condition. In figure 4*a* the revised axial ratio gives the values of θ_k indicated by circles. These circles are distributed roughly within an acute triangle, the apex of which lies at $\sin 2\theta/2\theta = 0$, $\theta = 90^\circ$. The downward slope from right to left is due to a systematic eccentricity error. The deviation of the circles from a straight line is due to individual errors of measurement, which are greatest at the lowest angles. By extrapolation to $\sin 2\theta/2\theta = 0$ it is seen that the most probable value of θ_k for this camera is 82.77° with a probable error of not more than 0.005° .

If the method were sound it should be possible by repeating the process in

another camera to obtain the same value for the axial ratio. The results of this experiment are shown in table 2 and figure 4*b*. The θ_k values represented by crosses are calculated for $c/a = 1.0999$, and show the same systematic deviation as in the upper figure. The circles for $c/a = 1.10002$ are much more consistent, and it therefore seems probable that this is the true value for the axial ratio. By extrapolation we get 82.51° for the most probable value of θ_k for the second camera.

Table 2. Calibration of camera 2

h, k, l	Radiation	Observed S (cm.)	Axial ratio $c/a = 1.0999$		Axial ratio $c/a = 1.10002$	
			θ^*	θ_k or $\theta S_k/S$	θ^*	θ_k or $\theta S_k/S$
412	α_1	19.437	61.313	82.606	61.312	82.605
	α_2	19.534	61.575	82.547	61.574	82.546
305	α_1	20.178	63.648	82.603	63.640	82.592
	α_2	20.270	63.938	82.603	63.930	82.592
116	α_1	20.815	65.636	82.576	65.624	82.561
	α_2	20.912	65.954	82.591	65.942	82.576
501	α_1	21.058	66.400	82.573	66.399	82.571
	α_2	21.163	66.729	82.571	66.729	82.570
404	α_1	21.302	67.175	82.580	67.169	82.572
	α_2	21.404	67.517	82.605	67.511	82.597
206	α_1	21.637	68.243	82.504	68.220	82.577
	α_2	21.754	68.603	82.584	68.590	82.567
413	α_1	21.870	68.965	82.579	68.961	82.573
	α_2	21.992	69.340	82.567	69.336	82.562
330	α_1	22.259	70.173	82.556	70.173	82.556
	α_2	22.382	70.573	82.571	70.573	82.570
502 } 225 }	α_1	22.724	71.650	82.568	71.646	82.564
	α_2	22.864	72.080	82.556	72.078	82.554
331	α_1	23.000	72.522	82.571	72.522	82.571
	α_2	23.261	73.332	82.556	73.332	82.556
420	α_1	23.416	73.816	82.551	73.816	82.551
	α_2	23.829	75.122	82.555	75.100	82.541
315	α_1	23.986	75.629	82.569	75.622	82.561
	α_2	24.161	76.154	82.540	76.154	82.540
234	α_1	24.359	76.799	82.562	76.700	82.553
	α_2	24.561	77.423	82.548	77.413	82.538
216	α_1	24.931	78.600	82.560	78.576	82.535
	α_2	25.164	79.332	82.557	79.307	82.531
End of film:		26.187 (S_k)				

Extrapolated value for $\theta_k = 82.51^\circ$, using $c/a = 1.10002$.

* Values of θ calculated from Bergqvist's d value with correction for refraction.

The axial ratio of quartz is much nearer 1.10002 than 1.0999. We now have the following values:

$$a = 4902.88 \text{ X. (calculated from Bergqvist)}$$

$$c = 5393.27 \pm 0.1 \text{ X.}$$

$$c/a = 1.10002 \pm 0.00004.$$

§6. EXPERIMENTS WITH OTHER SPECIMENS OF QUARTZ

The above data are valid for the particular specimen of quartz used in our calibration experiments. It was interesting to see whether the same values would be obtained from other specimens. One of the cameras calibrated in the above experiments was used to take photographs from a number of different quartz crystals, the temperature being maintained at 18° during each exposure.

Table 3. Clear quartz (Cornwall)

h, k, l	Radiation	S (cm.)	θ (degrees)	Lattice spacing of 100 planes (\AA .)
305	$\left\{ \begin{array}{l} \alpha_1 \\ \alpha_2 \end{array} \right.$	$\begin{array}{l} 20.220 \\ 20.314 \end{array}$	$\begin{array}{l} 63.632 \\ 63.927 \end{array}$	$\begin{array}{l} 4246.3 \\ .2 \end{array} \left. \vphantom{\begin{array}{l} 4246.3 \\ .2 \end{array}} \right\} 4246.3$
116	$\left\{ \begin{array}{l} \alpha_1 \\ \alpha_2 \end{array} \right.$	$\begin{array}{l} 20.848 \\ 20.953 \end{array}$	$\begin{array}{l} 65.608 \\ 65.938 \end{array}$	$\begin{array}{l} 4246.6 \\ .2 \end{array} \left. \vphantom{\begin{array}{l} 4246.6 \\ .2 \end{array}} \right\} 4246.4$
206	$\left\{ \begin{array}{l} \alpha_1 \\ \alpha_2 \end{array} \right.$	$\begin{array}{l} 21.678 \\ 21.791 \end{array}$	$\begin{array}{l} 68.220 \\ 68.575 \end{array}$	$\begin{array}{l} 4246.3 \\ .5 \end{array} \left. \vphantom{\begin{array}{l} 4246.3 \\ .5 \end{array}} \right\} 4246.4$
413	$\left\{ \begin{array}{l} \alpha_1 \\ \alpha_2 \end{array} \right.$	$\begin{array}{l} 21.909 \\ 22.031 \end{array}$	$\begin{array}{l} 68.947 \\ 69.331 \end{array}$	$\begin{array}{l} 4246.4 \\ .2 \end{array} \left. \vphantom{\begin{array}{l} 4246.4 \\ .2 \end{array}} \right\} 4246.3$
330	$\left\{ \begin{array}{l} \alpha_1 \\ \alpha_2 \end{array} \right.$	$\begin{array}{l} 22.297 \\ 22.422 \end{array}$	$\begin{array}{l} 70.168 \\ 70.561 \end{array}$	$\begin{array}{l} 4246.15 \\ .4 \end{array} \left. \vphantom{\begin{array}{l} 4246.15 \\ .4 \end{array}} \right\} 4246.2$
$\left. \begin{array}{l} 502 \\ 225 \end{array} \right\}$	$\left\{ \begin{array}{l} \alpha_1 \\ \alpha_2 \end{array} \right.$	$\begin{array}{l} 22.763 \\ 22.900 \end{array}$	$\begin{array}{l} 71.634 \\ 72.065 \end{array}$	$\begin{array}{l} 4246.3 \\ .3 \end{array} \left. \vphantom{\begin{array}{l} 4246.3 \\ .3 \end{array}} \right\} 4246.3$
331	$\left\{ \begin{array}{l} \alpha_1 \\ \alpha_2 \end{array} \right.$	$\begin{array}{l} 23.043 \\ 23.300 \end{array}$	$\begin{array}{l} 72.515 \\ 73.324 \end{array}$	$\begin{array}{l} 4246.2 \\ .15 \end{array} \left. \vphantom{\begin{array}{l} 4246.2 \\ .15 \end{array}} \right\} 4246.2$
420	$\left\{ \begin{array}{l} \alpha_1 \\ \alpha_2 \end{array} \right.$	$\begin{array}{l} 23.454 \\ 23.864 \end{array}$	$\begin{array}{l} 73.809 \\ 75.099 \end{array}$	$\begin{array}{l} 4246.2 \\ .15 \end{array} \left. \vphantom{\begin{array}{l} 4246.2 \\ .15 \end{array}} \right\} 4246.2$
315	$\left\{ \begin{array}{l} \alpha_1 \\ \alpha_2 \end{array} \right.$	$\begin{array}{l} 24.026 \\ 24.026 \end{array}$	$\begin{array}{l} 75.609 \\ 75.609 \end{array}$	$\begin{array}{l} 4246.2 \\ .25 \end{array} \left. \vphantom{\begin{array}{l} 4246.2 \\ .25 \end{array}} \right\} 4246.2$
421	$\left\{ \begin{array}{l} \alpha_1 \\ \alpha_2 \end{array} \right.$	$\begin{array}{l} 24.200 \\ 24.399 \end{array}$	$\begin{array}{l} 76.156 \\ 76.783 \end{array}$	$\begin{array}{l} 4246.1 \\ .0 \end{array} \left. \vphantom{\begin{array}{l} 4246.1 \\ .0 \end{array}} \right\} 4246.1$
234	$\left\{ \begin{array}{l} \alpha_1 \\ \alpha_2 \end{array} \right.$	$\begin{array}{l} 24.596 \\ 24.966 \end{array}$	$\begin{array}{l} 77.403 \\ 78.567 \end{array}$	$\begin{array}{l} 4246.1 \\ .2 \end{array} \left. \vphantom{\begin{array}{l} 4246.1 \\ .2 \end{array}} \right\} 4246.15$
216	$\left\{ \begin{array}{l} \alpha_1 \\ \alpha_2 \end{array} \right.$	$\begin{array}{l} 25.200 \\ 25.200 \end{array}$	$\begin{array}{l} 79.303 \\ 79.303 \end{array}$	$\begin{array}{l} 4246.15 \\ .05 \end{array} \left. \vphantom{\begin{array}{l} 4246.15 \\ .05 \end{array}} \right\} 4246.1$
End of film:		26.219 (S_k)	82.51 (θ_k)	

Extrapolated values of d_{100} : $4246.06 \pm 0.05 \text{ \AA}$.

The experiments fall into two groups. First two clear crystals were examined, and the results are given in tables 3 and 4, and in figures 5*a* and *b*. The tables show the measured values of S with the values of θ deduced from them, and for each line a value of the lattice spacing is calculated from them. To eliminate systematic errors the procedure described in our earlier paper was used. A value of the lattice spacing is deduced for each line, and the weighted mean for each K_α doublet is then plotted against the appropriate value of $\cos^2 \theta$. The points should lie near a straight line, which gives the correct value of the lattice spacing by extrapolation to $\cos^2 \theta = 0$. This method is directly applicable only to cubic crystals, where there is only one variable. For hexagonal crystals, where there are two variables a and c , one of these

Table 4. Clear quartz (St Gothard)

<i>h, k, l</i>	Radiation	<i>S</i> (cm.)	θ (degrees)	Lattice spacing of 100 planes (X.)	
305	$\left\{ \begin{smallmatrix} \alpha_1 \\ \alpha_2 \end{smallmatrix} \right.$	20.203	63.619	4246.8	} 4246.8
		20.296	63.912	.7	
116	$\left\{ \begin{smallmatrix} \alpha_1 \\ \alpha_2 \end{smallmatrix} \right.$	20.835	65.608	4246.6	} 4246.6
		20.934	65.921	.7	
206	$\left\{ \begin{smallmatrix} \alpha_1 \\ \alpha_2 \end{smallmatrix} \right.$	21.659	68.204	4246.7	} 4246.7
		21.775	68.569	.6	
413	$\left\{ \begin{smallmatrix} \alpha_1 \\ \alpha_2 \end{smallmatrix} \right.$	21.894	68.944	4246.5	} 4246.6
		22.011	69.313	.7	
330	$\left\{ \begin{smallmatrix} \alpha_1 \\ \alpha_2 \end{smallmatrix} \right.$	22.281	70.163	4246.3	} 4246.3
		22.406	70.556	.4	
502 } 225 }	$\left\{ \begin{smallmatrix} \alpha_1 \\ \alpha_2 \end{smallmatrix} \right.$	22.745	71.624	4246.6	} 4246.4
		22.887	72.071	.2	
331	$\left\{ \begin{smallmatrix} \alpha_1 \\ \alpha_2 \end{smallmatrix} \right.$.2	
		23.027	72.512		
420	$\left\{ \begin{smallmatrix} \alpha_1 \\ \alpha_2 \end{smallmatrix} \right.$	23.284	73.321	4246.2 ₅	} 4246.2 ₅
		23.438	73.806	.2 ₅	
315	$\left\{ \begin{smallmatrix} \alpha_1 \\ \alpha_2 \end{smallmatrix} \right.$	23.848	75.097	4246.2 ₅	} 4246.3
		24.010	75.607	.3	
421	$\left\{ \begin{smallmatrix} \alpha_1 \\ \alpha_2 \end{smallmatrix} \right.$.4	
		24.177	76.113		
234	$\left\{ \begin{smallmatrix} \alpha_1 \\ \alpha_2 \end{smallmatrix} \right.$	24.382	76.779	4246.2	} 4246.2
		24.581	77.405	.1 ₅	
216	$\left\{ \begin{smallmatrix} \alpha_1 \\ \alpha_2 \end{smallmatrix} \right.$	24.950	78.567	4246.1 ₅	} 4246.1
		25.174	79.304	.0 ₅	
End of film:		26.202 (<i>S_k</i>)	82.51 (θ_k)		

Extrapolated value of *d*₁₀₀: 4245.9₅ ± 0.05 X.

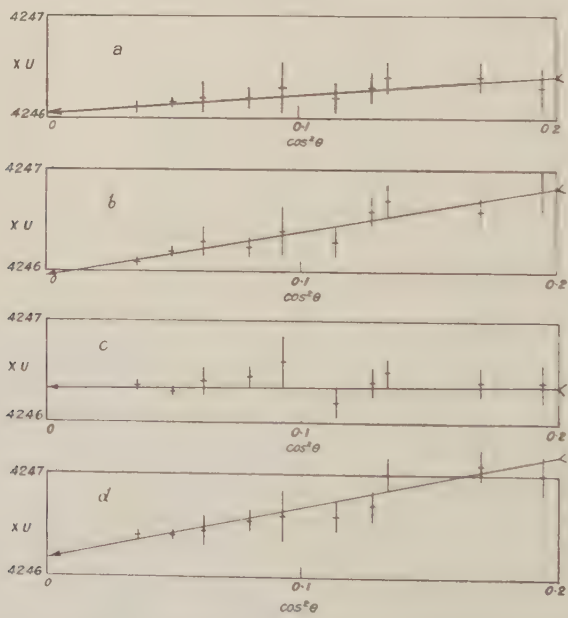


Figure 5. Lattice spacing of four specimens of quartz by extrapolation.

- a*

Clear quartz (Cornwall)

4246.0₅ X.

b

Clear quartz (St Gothard)

4245.9₅ X.
- c*

Milky quartz (Durham)

4246.3₀ X.

d

Rose quartz (Bohemia)

4246.2₀ X.

must be eliminated before the graphical method is applied. To this end we assume a value for the axial ratio and determine the (100) spacing for each line.

In the present experiments we assumed that $c/a = 1.10002$, and deduced a value of the spacing for each line. In figure 5 the weighted mean for each doublet is plotted against the appropriate value of $\cos^2 \theta$. The probable accuracy of each value is indicated by the length of the line. There is no systematic deviation of points for planes with different values of l , which would if present show that the axial ratio

Table 5. Milky quartz (Durham)

h, k, l	Radiation	S (cm.)	θ (degrees)	Lattice spacing of 100 planes (X.)
305	$\left\{ \begin{array}{l} \alpha_1 \\ \alpha_2 \end{array} \right.$	20.221 20.315	63.627 63.923	$4246.5 \left. \begin{array}{l} \\ .3 \end{array} \right\} 4246.4$
116	$\left\{ \begin{array}{l} \alpha_1 \\ \alpha_2 \end{array} \right.$	20.853 20.951	65.616 65.924	$4246.3 \left. \begin{array}{l} \\ .6 \end{array} \right\} 4246.4$
206	$\left\{ \begin{array}{l} \alpha_1 \\ \alpha_2 \end{array} \right.$	21.679 21.793	68.215 68.574	$4246.5 \left. \begin{array}{l} \\ .5 \end{array} \right\} 4246.5$
413	$\left\{ \begin{array}{l} \alpha_1 \\ \alpha_2 \end{array} \right.$	21.912 22.032	68.948 69.326	$4246.4 \left. \begin{array}{l} \\ .3 \end{array} \right\} 4246.4$
330	$\left\{ \begin{array}{l} \alpha_1 \\ \alpha_2 \end{array} \right.$	22.299 22.421	70.166 70.550	$4246.2 \left. \begin{array}{l} \\ .6 \end{array} \right\} 4246.3$
502 } 225 }	$\left\{ \begin{array}{l} \alpha_1 \\ \alpha_2 \end{array} \right.$	22.763 22.899	71.626 72.054	$4246.5 \left. \begin{array}{l} \\ .6 \end{array} \right\} 4246.6$
331	$\left\{ \begin{array}{l} \alpha_1 \\ \alpha_2 \end{array} \right.$	23.039	72.494	$4246.4 \left. \begin{array}{l} \\ .5 \end{array} \right\} 4246.45$
420	$\left\{ \begin{array}{l} \alpha_1 \\ \alpha_2 \end{array} \right.$	23.300 23.451	73.316 73.791	$4246.4 \left. \begin{array}{l} \\ .35 \end{array} \right\} 4246.4$
315	$\left\{ \begin{array}{l} \alpha_1 \\ \alpha_2 \end{array} \right.$	23.864 24.028	75.090 75.606	$4246.4 \left. \begin{array}{l} \\ .35 \end{array} \right\} 4246.4$
421	$\left\{ \begin{array}{l} \alpha_1 \\ \alpha_2 \end{array} \right.$	24.194	76.129	$4246.35 \left. \begin{array}{l} \\ .2 \end{array} \right\} 4246.3$
234	$\left\{ \begin{array}{l} \alpha_1 \\ \alpha_2 \end{array} \right.$	24.398 24.599	76.771 77.403	$4246.35 \left. \begin{array}{l} \\ .2 \end{array} \right\} 4246.3$
216	$\left\{ \begin{array}{l} \alpha_1 \\ \alpha_2 \end{array} \right.$	24.965 25.197	78.555 79.285	$4246.35 \left. \begin{array}{l} \\ .35 \end{array} \right\} 4246.35$
End of film:		26.222 (S_k)	82.51 (θ_k)	

Extrapolated value of d_{100} : 4246.30 ± 0.05 X.

was incorrect. It may be concluded that the axial ratio of the two new specimens of quartz is 1.10002 as in the former experiment. The points lie very close to a straight line, which, on extrapolation, gives for d_{100} the value 4246.05 ± 0.05 X. and 4245.95 ± 0.05 X. respectively, proving that the lattice spacing of quartz is identical in the three *clear* crystals examined to within 1 part in 50,000.

Further experiments were made with cloudy and coloured specimens. The results of two experiments with milky and coloured crystals respectively are given in tables 5 and 6 and in figures 5c and 5d. The following values were obtained:

For milky quartz $d_{100} = 4246.30 \pm 0.05$ X.

For rose quartz $d_{100} = 4246.20 \pm 0.05$ X.

The increase in spacing, though not great, definitely exceeds the experimental error. In experiments with crystals which were less uniformly or less distinctively marked a smaller increase in spacing was found. In no instance was there any indication of a different axial ratio.

Table 6. Rose quartz (Bohemia)

h, k, l	Radiation	S (cm.)	θ (degrees)	Lattice spacing of 100 planes (\AA .)
395	$\left\{ \begin{array}{l} \alpha_1 \\ \alpha_2 \end{array} \right.$	$\begin{array}{l} 20.197 \\ 20.293 \end{array}$	$\begin{array}{l} 63.610 \\ 63.912 \end{array}$	$\begin{array}{l} 4247.1 \\ 6.7 \end{array} \left. \vphantom{\begin{array}{l} 4247.1 \\ 6.7 \end{array}} \right\} 4247.0$
116	$\left\{ \begin{array}{l} \alpha_1 \\ \alpha_2 \end{array} \right.$	$\begin{array}{l} 20.825 \\ 20.927 \end{array}$	$\begin{array}{l} 65.587 \\ 65.909 \end{array}$	$\begin{array}{l} 4247.2 \\ .0 \end{array} \left. \vphantom{\begin{array}{l} 4247.2 \\ .0 \end{array}} \right\} 4247.1$
206	$\left\{ \begin{array}{l} \alpha_1 \\ \alpha_2 \end{array} \right.$	$\begin{array}{l} 21.653 \\ 21.767 \end{array}$	$\begin{array}{l} 68.195 \\ 68.554 \end{array}$	$\begin{array}{l} 4247.0 \\ .0 \end{array} \left. \vphantom{\begin{array}{l} 4247.0 \\ .0 \end{array}} \right\} 4247.0$
413	$\left\{ \begin{array}{l} \alpha_1 \\ \alpha_2 \end{array} \right.$	$\begin{array}{l} 21.887 \\ 22.010 \end{array}$	$\begin{array}{l} 68.933 \\ 69.320 \end{array}$	$\begin{array}{l} 4246.8 \\ .4 \end{array} \left. \vphantom{\begin{array}{l} 4246.8 \\ .4 \end{array}} \right\} 4246.7$
330	$\left\{ \begin{array}{l} \alpha_1 \\ \alpha_2 \end{array} \right.$	$\begin{array}{l} 22.272 \\ 22.403 \end{array}$	$\begin{array}{l} 70.145 \\ 70.558 \end{array}$	$\begin{array}{l} 4246.7 \\ .4 \end{array} \left. \vphantom{\begin{array}{l} 4246.7 \\ .4 \end{array}} \right\} 4246.6$
502 } 225 }	$\left\{ \begin{array}{l} \alpha_1 \\ \alpha_2 \\ \alpha_1 \end{array} \right.$	$\begin{array}{l} 22.739 \\ 22.879 \\ 22.879 \end{array}$	$\begin{array}{l} 71.616 \\ 72.056 \\ 72.056 \end{array}$	$\begin{array}{l} 4246.7 \\ .5 \\ .5 \end{array} \left. \vphantom{\begin{array}{l} 4246.7 \\ .5 \\ .5 \end{array}} \right\} 4246.6$
331	$\left\{ \begin{array}{l} \alpha_1 \\ \alpha_2 \end{array} \right.$	$\begin{array}{l} 23.021 \\ 23.276 \end{array}$	$\begin{array}{l} 72.504 \\ 73.307 \end{array}$	$\begin{array}{l} 4246.7 \\ .5 \end{array} \left. \vphantom{\begin{array}{l} 4246.7 \\ .5 \end{array}} \right\} 4246.55$
420	$\left\{ \begin{array}{l} \alpha_1 \\ \alpha_2 \end{array} \right.$	$\begin{array}{l} 23.430 \\ 23.842 \end{array}$	$\begin{array}{l} 73.792 \\ 75.090 \end{array}$	$\begin{array}{l} 4246.5 \\ .4 \end{array} \left. \vphantom{\begin{array}{l} 4246.5 \\ .4 \end{array}} \right\} 4246.55$
315	$\left\{ \begin{array}{l} \alpha_1 \\ \alpha_2 \end{array} \right.$	$\begin{array}{l} 24.005 \\ 24.169 \end{array}$	$\begin{array}{l} 75.603 \\ 76.120 \end{array}$	$\begin{array}{l} 4246.4 \\ .6 \end{array} \left. \vphantom{\begin{array}{l} 4246.4 \\ .6 \end{array}} \right\} 4246.45$
421	$\left\{ \begin{array}{l} \alpha_1 \\ \alpha_2 \end{array} \right.$	$\begin{array}{l} 24.375 \\ 24.573 \end{array}$	$\begin{array}{l} 76.769 \\ 77.392 \end{array}$	$\begin{array}{l} 4246.4 \\ .3 \end{array} \left. \vphantom{\begin{array}{l} 4246.4 \\ .3 \end{array}} \right\} 4246.4$
234	$\left\{ \begin{array}{l} \alpha_1 \\ \alpha_2 \end{array} \right.$	$\begin{array}{l} 24.941 \\ 25.174 \end{array}$	$\begin{array}{l} 78.551 \\ 79.285 \end{array}$	$\begin{array}{l} 4246.4 \\ .3 \end{array} \left. \vphantom{\begin{array}{l} 4246.4 \\ .3 \end{array}} \right\} 4246.4$
216	$\left\{ \begin{array}{l} \alpha_1 \\ \alpha_2 \end{array} \right.$	$\begin{array}{l} 25.174 \\ 26.198 \end{array}$	$\begin{array}{l} 79.285 \\ 82.51 \end{array}$	$\begin{array}{l} 4246.4 \\ .3 \end{array} \left. \vphantom{\begin{array}{l} 4246.4 \\ .3 \end{array}} \right\} 4246.4$
End of film:		$26.198(S_k)$	$82.51(\theta_k)$	

Extrapolated value of d_{100} : $4246.20 \pm 0.05 \text{ \AA}$.

§ 7. CONCLUSIONS

Our experiments have shown that quartz is a very suitable substance to use for the calibration of powder photograph cameras when this operation is performed in a preliminary experiment. It would scarcely be possible to use quartz in the mixture method owing to the large number of lines in the X-ray pattern. It has, however, been shown that by the authors' methods an accuracy of 1 part in 50,000 may be attained without mixing the powders.

Quartz gives with CuK_α radiation an extremely good powder photograph in which the K_α doublets at high angles may be clearly resolved and accurately measured. For convenience of reference the glancing angles of reflection θ for these lines are given in table 7, together with $\sin 2\theta$ which is required for the extrapolation process. The values given in this table are corrected for deviation from Bragg's law.

In the case of overlapping lines we have made an estimate of the angle corresponding to the centre of gravity of the reflection.

Table 7. Glancing angles for quartz, on the assumption that $a = 4902.88 \text{ \AA}$, $c = 5393.27 \text{ \AA}$.

h, k, l	Radiation	θ^*	$\sin 2\theta/2\theta$
216	$\left\{ \begin{matrix} \alpha_2 \\ \alpha_1 \end{matrix} \right\}$	$\left\{ \begin{matrix} 79.307 \\ 78.576 \end{matrix} \right\}$	0.238
234	$\left\{ \begin{matrix} \alpha_2 \\ \alpha_1 \end{matrix} \right\}$	$\left\{ \begin{matrix} 77.413 \\ 76.790 \end{matrix} \right\}$	0.282
421	$\left\{ \begin{matrix} \alpha_2 \\ \alpha_1 \end{matrix} \right\}$	$\left\{ \begin{matrix} 76.154 \\ 75.622 \end{matrix} \right\}$	0.319
315	$\left\{ \begin{matrix} \alpha_2 \\ \alpha_1 \end{matrix} \right\}$	$\left\{ \begin{matrix} 75.109 \\ 75.109 \end{matrix} \right\}$	0.371
420	$\left\{ \begin{matrix} \alpha_2 \\ \alpha_1 \end{matrix} \right\}$	$\left\{ \begin{matrix} 73.816 \\ 73.332 \end{matrix} \right\}$	0.406
331	$\left\{ \begin{matrix} \alpha_2 \\ \alpha_1 \end{matrix} \right\}$	$\left\{ \begin{matrix} 72.522 \\ 72.078 \end{matrix} \right\}$	0.451
225 } 502 }	$\left\{ \begin{matrix} \alpha_2 \\ \alpha_1 \end{matrix} \right\}$	$\left\{ \begin{matrix} 71.646 \\ 71.646 \end{matrix} \right\}$	0.483
330	$\left\{ \begin{matrix} \alpha_2 \\ \alpha_1 \end{matrix} \right\}$	$\left\{ \begin{matrix} 70.573 \\ 70.173 \end{matrix} \right\}$	0.501
413	$\left\{ \begin{matrix} \alpha_2 \\ \alpha_1 \end{matrix} \right\}$	$\left\{ \begin{matrix} 69.336 \\ 68.961 \end{matrix} \right\}$	0.530
206	$\left\{ \begin{matrix} \alpha_2 \\ \alpha_1 \end{matrix} \right\}$	$\left\{ \begin{matrix} 68.590 \\ 68.229 \end{matrix} \right\}$	0.549
404	$\left\{ \begin{matrix} \alpha_2 \\ \alpha_1 \end{matrix} \right\}$	$\left\{ \begin{matrix} 67.511 \\ 67.169 \end{matrix} \right\}$	0.571
501	$\left\{ \begin{matrix} \alpha_2 \\ \alpha_1 \end{matrix} \right\}$	$\left\{ \begin{matrix} 66.729 \\ 66.399 \end{matrix} \right\}$	0.623
116	$\left\{ \begin{matrix} \alpha_2 \\ \alpha_1 \end{matrix} \right\}$	$\left\{ \begin{matrix} 65.942 \\ 65.624 \end{matrix} \right\}$	0.685
305	$\left\{ \begin{matrix} \alpha_2 \\ \alpha_1 \end{matrix} \right\}$	$\left\{ \begin{matrix} 63.930 \\ 63.640 \end{matrix} \right\}$	
412	$\left\{ \begin{matrix} \alpha_2 \\ \alpha_1 \end{matrix} \right\}$	$\left\{ \begin{matrix} 61.574 \\ 61.312 \end{matrix} \right\}$	

* Corrected for refractivity.

Smoky and coloured crystals have a slightly larger spacing, and must be avoided for calibration work. Our results are not in agreement with a paper recently published by Yuchting Tu*. In an investigation of the lattice spacing of quartz he finds that the measurements from different faces of the same form (i.e. different 101 faces or different 100 faces) on the same crystal vary by as much as 1 per cent. For this reason he thinks that quartz is unsuitable as a standard for wave-length determinations. Yuchting Tu states that his crystals appear to be distorted. This is the probable explanation of the discrepancies. In our experiments only good crystals with smooth faces were used. Among 10 such crystals, all from different localities, we did not find one which failed to resolve the α doublets clearly and

* *Phys. Rev.* 40, 662 (1932).

distinctly, which would be impossible with variations of the order of 1 per cent. Moreover, in every case the measurements from different planes were consistent within the limits of experimental error; this is well shown by figure 5. The four examples selected in this diagram include the *biggest* differences in lattice spacing out of the 10 specimens measured.

In conclusion we give a summary of the steps in our method of lattice-spacing determination. (a) *Calibration of the camera.* An angle θ_1 characteristic of the camera is found from a powder photograph of quartz by means of equation (3) and the values of θ in table 7. If the values of θ_1 from different lines show a systematic divergence, they are plotted against $\sin 2\theta$ and extrapolated to $\sin 2\theta = 0$. (b) *Calculation of the glancing angles* for any substance, from powder photograph measurements and the camera constant θ_1 . (c) *Deduction of lattice spacing.* From each θ value the lattice spacing is deduced. If the crystal is hexagonal, trigonal or tetragonal* an approximate value of the axial ratio is assumed and only one of the lattice spacings (d) is found for each line. The value of d for each α doublet is then plotted against the appropriate value of $\cos^2 \theta$ and the points are extrapolated to $\cos^2 \theta = 0$. This gives the most probable value of the lattice spacing. If the values of d show a systematic divergence from a straight line the axial ratio is incorrect and must be adjusted. It is, however, important to confine measurements as far as possible to values of θ between 60° and 90° for accurate work.

By the above methods it is possible to obtain very accurate values of lattice spacings from photographs in circular cameras of diameter 9 cm. This has the advantage of requiring only a short time of exposure, and moreover a complete powder photograph which may be useful for other purposes is obtained at the same time as the accurate lattice-spacing determination.

§ 8. ACKNOWLEDGMENTS

In conclusion we desire to thank Professor W. L. Bragg, F.R.S., for his encouraging interest in the work, which was carried out in the Physical Laboratories of the University of Manchester. We also thank Mr A. P. M. Fleming, C.B.E., Director-Manager, Research and Education Departments of the Metropolitan-Vickers Elec. Co. Ltd., for his kind and helpful interest. We are indebted to Dr H. E. Buckley and Dr J. W. Jackson for the specimens of quartz.

* The method may be extended to orthorhombic crystals where the approximate values of the axial ratios are known.

THE THERMAL CONDUCTIVITY OF WATER

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ABSTRACT. The paper describes the precise measurement of the thermal conductivity of water in a range of temperatures extending from 7° C. to 60° C. The parallel-plate method has been employed, the apparatus being especially designed to cope with the difficulties which arise in the measurement of the conductivity of a volatile liquid. Two series of measurements were made, the plates in one apparatus having approximately three times the area of those in the other.

§ 1. PREVIOUS MEASUREMENTS

IN the past the hot-wire method and the parallel-plate method have been used to measure the conductivity of liquids. The use of the first has been confined principally to relative measurements as very narrow tubes must be employed to prevent convection and it is (Goldschmidt)* impossible to determine with sufficient accuracy the geometry of the apparatus. In previous plate experiments the corrections applied have usually been considerable, and the results obtained do not agree within the limits of the claimed accuracy of the separate measurements.

The work previous to 1920 has been critically discussed by Jacob†. Notable among these early experiments is that of Lees‡, who developed the plate method and found, by means of it, that water possessed a relatively large negative temperature coefficient of thermal conductivity. Jacob himself carried out an extensive series of measurements and obtained definite evidence of a positive coefficient. This result has since been confirmed by Bridgman§, Davis||, and Kay and Higgins¶, but the actual magnitude of the coefficient still remains uncertain, the values found lying within the range 0.001 to 0.003. A similar lack of agreement exists in the values given to the conductivity at 0° C. These range from 1.32×10^{-3} to 1.45×10^{-3} cal./sec.-deg.-cm. It is possible that this lack of agreement is due in part to the fact that, with the exception of Jacob's experiments, the investigations on water have been incidental to other problems. In view of the fundamental importance of water, both from the point of view of theory and practice, the authors felt that further work on it was justified.

* *Phys. Z.* **12**, 417 (1911).

† *Phil. Trans. A*, **191**, 399 (1898).

|| *Phil. Mag.* **47**, 1057 (1924).

† *Ann. d. Phys.* **4**, 63, 537 (1920).

§ *Proc. Nat. Acad. Sci.* **9**, 341 (1923).

¶ *Proc. R. S. A*, **117**, 459 (1928).

§ 2. PRINCIPLE OF THE METHOD

A film of water is formed between two parallel plates, the bottom one being held at a constant temperature by water-circulation while the upper one is heated electrically. Since the upper plate is hotter than the lower there can be no convection, provided the film is horizontal. Loss of heat by the top plate to the surroundings is prevented by a guard dome, which is maintained at a slightly higher temperature than the top plate.

Assuming a normal flow of heat through the water film from the electrically heated top plate to the bottom plate,

$$E_1 E_2 / JR = k.A.\Delta\theta/2a + L + E,$$

where

E_1	E_1 is the p.d. across the heating coil;
E_2, R	E_2 the p.d. across a standard series resistance R ;
k	k cal./sec.-deg.-cm. the coefficient of thermal conductivity;
A	A the area of each plate;
L	L the rate of loss of heat to the surroundings;
E	E the rate at which heat is used in the evaporation of water; and
	$\Delta\theta/2a$ the temperature-gradient in the film.

On account of evaporation, especially at the higher temperatures, it is difficult to maintain the free surface of the liquid perpendicular to the plates. A calculation was therefore made of the effect of curved edges to the film. Suppose $ABCD$, figure 1, to be a vertical diametral section of the liquid film, the section AB of the free surface being part of a circle of radius R . The thickness of the film is $2a$, the diameter of the plates $2r$.

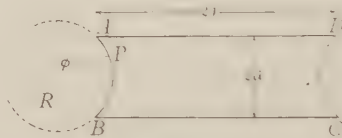


Figure 1.

Consider the heat-flow across a section of the film parallel to the plates through any point P . Assuming that there is no lateral heat-loss the equation of the heat-flow is

$$\frac{\partial}{\partial x} \left(sk \frac{\partial \theta}{\partial x} \right) = 0 \quad \dots\dots(1),$$

θ, x, s where θ is the temperature at a distance x from the top plate and s is the area of the section.

$$\text{This gives} \quad sk/R \sin \phi = Q \partial \phi / \partial \theta \quad \dots\dots(2),$$

Q where Q calories is the quantity of heat passing any section per second.

$$\text{Hence} \quad k \frac{\partial \theta}{\partial \phi} = \frac{QR \sin \phi}{\pi \{r - R \sin \phi + \sqrt{(R^2 - a^2)}\}}$$

$$\text{and} \quad \pi k \Delta\theta = \frac{2a.b.Q}{r(b^2 - R^2)} + \frac{2R^2 Q}{(b^2 - R^2)^{\frac{3}{2}}} \tan^{-1} \frac{a \sqrt{(b^2 - R^2)}}{b \sqrt{(R^2 - a^2)} - R^2} \quad \dots\dots(3),$$

where $\Delta\theta$ is the temperature-difference between the plates and $b = r + \sqrt{(R^2 - a^2)}$. For a straight edge ($R \rightarrow \infty$) this becomes

$$\pi k \Delta\theta = 2aQ/r^2. \quad \dots\dots(4).$$

This is the expression used for k when the curvature at the edges is neglected. It can be shown that if the free surface is convex outwards the expression is

$$\pi k \Delta\theta = \frac{2a \cdot b \cdot Q}{r(b^2 - R^2)} - \frac{2R^2 Q}{(b^2 - R^2)^{\frac{3}{2}}} \tan^{-1} \frac{a \sqrt{(b^2 - R^2)}}{b \sqrt{(R^2 - a^2)} + R^2} \quad \dots\dots(5).$$

§ 3. APPARATUS

Two sets of apparatus of different dimensions were used, both having a common design shown in figure 2. The liquid film was formed between the surfaces of the cold plate P and the heater unit H , the latter being supported on P by three cylindrical glass pillars each 0.1070 cm. high. Both hot and cold plates were of electrolytic copper, scraped flat and gilded, and were finally tested for flatness against optically flat glass. The plates were 3.460 cm. in diameter in one apparatus and 6.00 cm. in the other. The temperatures of these plates were measured with thermocouples embedded in holes some 2 mm. from each surface and reaching to the centres of the plates.

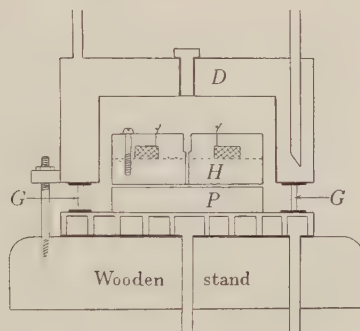


Figure 2.

The cold plate P was maintained at a constant temperature by a uniform flow of water through a helical groove cut in the bottom of the plate. The water supply was maintained from a large copper reservoir, both reservoir and leads being heavily insulated.

The heater H was a solid copper cylinder in which was embedded a heating-coil of manganin wire of approximately 16Ω resistance. This heater was surrounded by a hollow dome D of heavy sheet copper maintained at a uniform temperature by a constant flow of water from a second reservoir. A removable solid copper plug was provided in the top of the dome to replenish the liquid film if necessary during the course of a run.

In order to reduce the evaporation of the film to a minimum it was enclosed in an airtight space by supporting the dome on a glass ring G which rested on the cold

plate P , the surface of contacts between the glass and metal being sealed with rubber gaskets. The leads to the thermocouples and heating-coil were brought out through these gaskets. In this manner it was possible to saturate the air near the film at the high temperatures, where the evaporation would normally have become unmanageably large, and still keep the film under observation. The film was formed by allowing drops of boiled distilled water to run down a central hole in the heater, bubbles being prevented by lightly packing the hole with lint.

The whole of the apparatus was enclosed in a constant temperature enclosure, consisting of a wooden box lined with thick layers of cotton wool and having glass windows for viewing the film.

§ 4. MEASUREMENTS OF TEMPERATURES

All temperature-measurements were made with copper-constantan thermoelements, whose e.m.f.s. were measured by means of a Wolff potentiometer. Ten microvolts produced a deflection of five divisions on the galvanometer scale, and since it was possible to read this to one tenth of a division, temperatures could be read to better than 0.01°C . The temperature-difference between the dome and the heater was measured by means of a differential couple, while that between the two plates was measured in some cases with a couple used differentially and in others with two separate couples.

The couples were first tested for homogeneity and then calibrated by comparison with a platinum resistance thermometer, whose constants had previously been very carefully determined*, and whose fundamental interval was once again checked to ensure that no change had occurred since its previous calibration. The calculations of temperatures from e.m.f.s. were made by Adams' method†.

§ 5. MEASUREMENT OF POWER

The power supplied to the heating-coil was calculated from the measurement of the potential drop E_1 across the heating-coil and that E_2 across a standard resistance of nominal value 0.1Ω . The rate of heat-generation was equal to

$$E_1 E_2 / 4.18 \times 0.09998 \text{ cal./sec.}$$

§ 6. CORRECTIONS

Effect of curvature of the free surface of the water film. On substituting the dimensions of the apparatus used in equation (5) it was found that a radius of curvature of approximately 2 mm. would produce a change of 1 per cent in the value of k deduced in the less favourable case, that of the smaller apparatus. The film was therefore viewed constantly during a run and the final temperatures were taken when the surface was perpendicular to the plates. At the highest temperatures,

* T. H. Laby and E. O. Hercus, *Phil. Trans. (A)*, **227**, 63 (1927). We are indebted to Dr Hercus for assistance in calibrating the thermocouples.

† *Amer. Inst. Mining and M. Eng.* p. 165 (1920).

where this was sometimes difficult to arrange, the values of k were checked by using equations (3) and (5).

Heat-losses. If conditions are steady so that the thermal capacity of the apparatus does not have to be considered,

$$kA\Delta\theta/0.107 = E_1E_2/4.18 \times 0.09998 - L - E,$$

where L is made up of separate heat-losses H_1 , H_2 , H_3 , and H_4 .

H_1 cal./sec. is the heat lost from the heater to the dome per second. As the dome is always kept at a slightly higher temperature than the heater, only conduction has to be considered. The air space was considered as equivalent to that between two concentric cylinders of radii r and b respectively and length $\frac{1}{2}(L + l)$, together with that between two parallel discs of radii r and b and $(L - l)$ apart.

$$H_1 = \pi k_a \Delta t \left(\frac{L + l}{\log_e(b/r)} + \frac{rb}{L - l} \right).$$

k_a^* was taken as $5.33 \times 10^{-5} (1 + 0.003\theta)$.

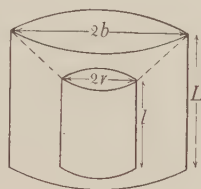


Figure 3.

Δt is the temperature-difference between the heater and the dome and is always negative. For the small apparatus H_1 has values ranging from 0.003 to 0.006, while for the large apparatus, owing to a greater difference $(L - l)$, the values are approximately one tenth as great.

H_2 cal./sec. is the heat radiated per second from the top to the bottom plate. The emissivity of the gilded surfaces compared with that of a black body was found to be 0.12 and as the maximum value of H_2 attained was 0.0001, H_2 could be neglected. H_3 cal./sec. is the heat conducted per second through the glass pillars which have a total cross section 0.0239 cm.² and length 0.1070 cm.

$$H_3 = 3.64 \times 10^{-4} \Delta\theta.$$

H_4 cal./sec. is the heat conducted per second along the leads from the heater to the constant-temperature enclosure.

$$H_4 = 3.14 \times 10^{-5} \delta\theta,$$

where $\delta\theta$ is the temperature-difference between the heater and the enclosure. This correction had a maximum value of the order 0.0006 at the highest temperature.

In the case of the larger apparatus a correction was made for any slight change in temperature of the heaters during an experiment.

* *International Critical Tables*, 5.

In order to test the validity of the above corrections and to see whether there was any large heat-loss unaccounted for, a measurement was made of the conductivity of air with each apparatus. 6.1×10^{-5} was obtained at 0°C. , a value somewhat greater than recent values (Trautz and Zündel)* which are of the order of 5.7×10^{-5} but considering the unsuitability of the apparatus for measuring such small conductivities the result must be regarded as satisfactory. A considerable variation is to be found in the literature for the conductivity of air at 0°C. , but it seems certain that in these water experiments the amount of heat unaccounted for is less than 1 per cent.

Table 1

$\theta (^\circ \text{C.})$	$\frac{E_1 E_2}{JR}$	L	E	$\Delta\theta$	$k \times 10^3$	$k \times 10^3$ (calculated)
10.0	.4468	— .00411	—	3.61	1.426	1.426
13.5	.4421	— .00357	—	3.55	1.434	1.437
14.4	.5944	— .00188	—	4.73	1.438	1.440
16.1	.5968	— .00253	—	4.71	1.452	1.446
17.9	.6013	— .00246	—	4.72	1.460	1.451
19.8	.5879	— .00206	—	4.60	1.464	1.457
20.7	.4606	— .00232	—	3.62	1.459	1.460
20.9	.4524	— .00349	—	3.55	1.466	1.461
24.5	.5957	— .00430	—	4.64	1.476	1.472
25.1	.5224	— .00372	—	4.08	1.472	1.474
25.9	.4236	— .00141	—	3.27	1.484	1.477
26.6	.5917	— .00342	—	4.60	1.477	1.479
28.4	.5883	— .00208	—	4.57	1.474	1.485
29.4	.4687	— .00328	.0023	3.60	1.489	1.488
29.9	.5857	— .00256	.0023	4.45	1.503	1.490
30.8	.4647	— .00314	.0062	3.51	1.501	1.493
34.2	.4720	— .00302	.0079	3.56	1.497	1.503
36.1	.4808	— .00180	.0081	3.59	1.509	1.506
39.1	.4647	— .00322	.0073	3.44	1.529	1.519
42.6	.4744	— .00093	.0090	3.51	1.517	1.530
47.0	.5776	— .00610	.0099	4.22	1.552	1.545
47.4	.5842	— .00179	.0099	4.29	1.532	1.546
50.2	.4275	— .00137	.0046	3.10	1.563	1.555
54.1	.4315	— .00280	.0111	3.08	1.565	1.567
60.3	.4315	— .00348	.0196	2.99	1.585	1.587

Table 2

$\theta (^\circ \text{C.})$	$\frac{E_1 E_2}{JR}$	L	E	$\Delta\theta$	$k \times 10^3$	$k \times 10^3$ (calculated)
7.4	1.008	.002	—	2.71	1.406	1.418
21.5	1.014	.002	—	2.62	1.403	1.403
34.6	1.271	.003	.0164	3.14	1.510	1.505
49.8	1.007	.006	.0267	2.36	1.563	1.555

Evaporation correction. E cal. sec. represents the rate at which heat is being used in evaporation of the water at the free surface. This was calculated from observation of the rate of change of the curvature of the meniscus and the known

* *Z. f. tech. Phys.* 6, 280 (1931).

latent heat of evaporation at the temperature. Depending as it does on the degree of saturation of the air space the magnitude of this correction varied somewhat irregularly from experiment to experiment.

§ 7. RESULTS

Tables 1 and 2 show the relevant details of the experiments on water with the small and large apparatus respectively. The authors' results can be best represented by

$$k \times 10^3 = 1.394 (1 + 0.0023t),$$

the mean departure from this being 0.4 per cent and the maximum departure less than 1 per cent. They are compared with those of previous workers in table 3, where values of k at 0°, 15° and 60° C. and the temperature coefficient α are shown.

Table 3

	$10^5 \times k$ at			α
	0° C.	15° C.	60° C.	
Jacob	132	138	156	.0030
Bridgman	134	139	154	.0022
Martin and Lang	139	144	159	.0023
Kaye and Higgins	145	148	156	.0012

The values of k given by different workers agree better at the higher temperatures. This is difficult to understand, as the most troublesome correction, that due to evaporation, does not enter seriously at the lower temperatures. The chief criticism which can be levelled against the previous work concerns the magnitude of the corrections involved. The evaporation correction in the case of Kaye and Higgins is very uncertain, and the thickness of the water layer, which in no case exceeded 0.5 mm. and fell as low as 0.25 mm., was rather small for the measurement of such relatively high conductivities. The presence of the gallery of liquid in their apparatus would also be expected to give high values of k . The total correction applied to the measured power by Jacob ranges from 2 per cent to 10 per cent. In the present experiments it was only twice above 2 per cent and was usually less than 1 per cent.

§ 8. ACKNOWLEDGMENT

In conclusion we wish to express our indebtedness to Prof. T. H. Laby for his constant interest and the helpful suggestions made during the course of the work.

THE MEASUREMENT OF THE VISCOSITY OF A MOLTEN METAL BY MEANS OF AN OSCILLATING DISC

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ABSTRACT. Experiments have been made on the viscosity of molten tin by the use of an oscillating disc. The theory of the method has been investigated, and it has been found necessary to calibrate the apparatus on molten metals having viscosities and densities not too different from those of the metals which are to be investigated. In the case of tin, the values of the viscosity at different temperatures have been determined by Sauerwald and Töpler by the capillary-tube method, and the present experiments have lengthened the range of temperature for which the viscosity of tin may be regarded as fairly well established. Discontinuity in the (viscosity, temperature) curve of molten tin at temperatures near its freezing point must be regarded as very improbable, and certainly does not occur at temperatures more than 6°C . above that point.

It has been shown that the method of the oscillating disc may be used in cases where other methods of measurement are inapplicable, but it is desirable to verify the measurements which have been made by Sauerwald and his co-workers by the capillary-tube method in order that full reliance may be placed on the values of the viscosities of the metals which are most suitable for the calibration of the oscillating-disc type of apparatus.

§ 1. GENERAL CONSIDERATIONS

PUBLISHED measurements of the viscosities of molten metals are scanty, and, for the most part, unconfirmed. Moreover, the reliable measurements have all been obtained by determining the pressure-difference required to drive a measured quantity of liquid per second through a capillary tube of known effective resistance. The viscosities which have been measured are all very small, the kinematic viscosities being usually considerably less than that of water, and in no case exceeding it. (The kinematic viscosity $\nu = \eta / \rho$, where η is the viscosity, and ρ the density.) There are but two other established methods of measurement which offer any hope of success in place of the capillary-tube method. These are the Couette or Margules method, and the logarithmic-decrement method. In the former it is necessary to determine the torque which must exist between two concentric cylinders, rotating at different velocities, when the annular space between the cylinders is filled with the liquid under investigation. For liquids of low kinematic viscosity, this method is difficult for a variety of reasons, and even in the case of water Couette was unable to dismantle his apparatus and reassemble it without producing a very considerable change in its constants. The added difficulties attendant on the use of high temperatures seem to rule out the use of this type of apparatus.

The logarithmic-decrement method is experimentally the simplest of all, the main difficulties being of a theoretical nature. As usually employed, it consists in the determination of the logarithmic decrements between successive maximum displacements of a solid of revolution which is immersed in the liquid, and executes, about its vertical axis of symmetry, rotational oscillations under the control of a torsion wire, or a bifilar suspension.

The theory of such an instrument is in its simplest form when the amplitudes of vibration are very small and the vessel containing the liquid is very large compared with the dimensions of the oscillating body. In the case of molten metals the inertia of the liquid is great compared with its viscosity, and the movements of the liquid contained in a very large vessel are inappreciable at comparatively small distances from the surface of the oscillating body. The variations in the rate of decay of the oscillations of the latter are, therefore, not seriously affected by small changes in the dimensions of the containing vessel or in the height of the liquid contained therein, nor is it necessary that the oscillating body should be very accurately placed in its proper position within the vessel. Those who are familiar with the peculiar difficulties of high-temperature work will realize the very great importance of these considerations with regard to the choice of a suitable method of measurement. In comparison with the capillary-tube method, the logarithmic-decrement method has also the advantage of permitting a considerable choice in the materials from which the oscillating body and the containing vessel are formed. Capillary tubes, on the other hand, can only be made of silica, or glass for very low temperatures, and if the containing vessel be friable, care must be exercised to prevent any particles of dust from entering the capillary tube. As silica is attacked by aluminium and certain other metals, the capillary-tube method is inapplicable to them. Owing to devitrification, silica tubes cannot be used at temperatures greatly in excess of 1100°C . Unfortunately, the logarithmic-decrement method has several disadvantages. In the first place, the theory underlying the measurements is very complex, and can be applied to absolute measurements only in circumstances which are experimentally inconvenient. Secondly, the actual design of an oscillating system is a matter of some delicacy, a compromise being necessary between a considerable number of conflicting requirements. To a smaller extent this remark applies also to the capillary-tube method.

§ 2. APPARATUS

As the work of Fawsitt* had demonstrated the practicability of the logarithmic-decrement method, it was decided to give this a trial. As an oscillating body a disc of alumina, somewhat thicker at the centre than at the periphery, was chosen. The slight taper in the section facilitates the escape of air bubbles which might adhere to the under surface of the disc if this surface were horizontal. The tapered disc is less liable to warp during drying and firing than one with parallel surfaces, and the extra thickness in the centre does not add very much to the volume. This is important, for it is desirable to use a body of such a shape that its volume is as small as possible for a given degree of damping of its oscillations. This is because the

* *Proc. R. S. A.*, **80**, 290 (1908).

buoyancy of the disc on immersion in the molten metal reduces the tension of the suspension wire, and raises the effective centre of gravity of the suspended system to an extent proportional to the density of the liquid in which it is immersed.

Although pure alumina was finally selected as a material for both the disc and the containing vessel, graphite was used in the early experiments, as the ease with which it could be machined rendered its use attractive. Unfortunately, it was found to disintegrate to a slight extent, and measurements in mercury were vitiated by the formation of a scum on the surface.

The suspended system finally adopted included the alumina disc, which had a diameter of 1.8 in., with a short stem of diameter $\frac{3}{16}$ in. fixed in a steel disc, $\frac{1}{4}$ in. thick and 3 in. in diameter, which acted as a sinker and as a mass of suitable moment of inertia. To the top of the steel disc was attached a steel rod, $\frac{3}{16}$ in. in diameter, extending upwards to the cold part of the furnace in which the experiments were

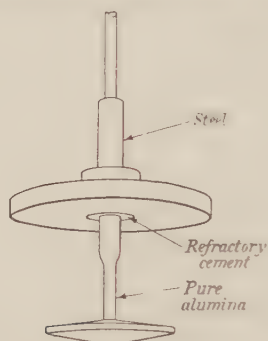


Figure 1. Construction of disc.

conducted. The top of this rod was fixed to the lower end of the torsion wire, which was of phosphor bronze, 0.006 in. in diameter, and rather less than a foot in length. The two discs are shown in figure 1. The period of a complete oscillation of the system was always very close to 28 sec. The upper end of the steel rod carried, in the earlier experiments, a light mirror, and later a light aluminium disc, 3 in. in diameter, having a rim bearing a scale divided into 500 parts extending all round the circumference.

The whole of this system, together with a pot of metal, could be enclosed in a wire-wound electric furnace in which an atmosphere of hydrogen was maintained. The furnace proper had an internal diameter of $3\frac{1}{4}$ in. and a length of 2 ft. The furnace tube, of silica, extended some 6 in. above the top of the furnace proper, this extension being water-cooled. A brass tube closed at its upper end was sealed to the top of the silica furnace tube, and formed a further extension in order to carry the torsion head. A window of optical glass was sealed into the brass tube at the level of the mirror, or the circular scale, thus permitting measurements to be made of the amplitudes of the oscillations with the aid of a telescope, a distant scale being used for the early experiments using the mirror, while direct readings of the divided scale were made during the later experiments.

Oscillations could be started and controlled by the rotation of the torsion head; as hydrogen was used in the apparatus, this entailed a gas-tight joint. The torsion wire was soldered at its upper end into a bronze rod $\frac{1}{4}$ in. in diameter, which was accurately fitted to a bronze sleeve some 5 in. long through which it passed. The rod was lubricated with vaseline, and a small cup was turned out of the top of the sleeve to act as a reservoir for lubricant. Such a joint, if well made, will hold a vacuum for a fortnight without the lubricant having to be replenished. It has the advantage of permitting vertical movements of the centre rod in addition to movements of rotation. The disc could therefore be lowered into the molten metal at the start of a series of measurements and raised from the metal at the end of the experiment. A simple arrangement enabled the rod to be clamped at the correct height when required, so that oscillations could be initiated by means of a rotary motion without disturbing the vertical adjustment.

The pot of metal was placed in the middle of the furnace on an inverted, closed hollow cylinder of refractory material filled with asbestos wool. This cylinder, occupying almost the whole width of the furnace tube, acted as an effective heat-insulator. A platinum-rhodium-platinum thermocouple, enclosed in a silica sheath, was inserted into the furnace from below through suitable apertures, a gas-tight joint being made at the bottom of the furnace. The top of the thermocouple sheath touched the bottom of the pot of metal. A similar heat-insulating cylinder, with a central tube of bore $\frac{1}{2}$ in. through which passed the rod carrying the discs, was suspended from the upper end of the furnace tube. The furnace winding was uniformly spaced, and therefore the variations of temperature in different parts of the free space, some 7 in. long in the middle of the furnace, were negligibly small. The current through the furnace was thermostatically controlled, and no appreciable changes of temperature occurred during a measurement of the logarithmic decrement.

§ 3. THEORY OF THE EXPERIMENTAL SYSTEM

We shall now consider the theory of these experiments when the maximum velocity of the disc is very small. In this case it is found by experiment that the logarithmic decrement of the amplitude of vibration is independent of the value of the amplitude.

The simplest equation of motion which yields this result may be written

$$K \frac{d^2 \theta}{dt^2} + \lambda \frac{d\theta}{dt} + n^2 \theta = 0 \quad \dots\dots(1), \quad t$$

where θ is the angular displacement of the disc, and K , λ , and n are constant during a series of oscillations. θ, K, λ, n

If Λ be the logarithmic decrement of a system conforming with this equation, Λ

$$\Lambda = \lambda T / 2K,$$

where T is the time of vibration of the system. T

Now equation (1) is known to apply to the case of an ellipsoid of revolution oscillating with a small amplitude about its generating axis in a fluid contained in a vessel which has also the shape of an ellipsoid of revolution having its generating axis

coincident with that of the oscillating body. It is therefore reasonable to assume that an equation of the form (1), with suitable values of K and λ , is applicable to the case of the disc and vessel used in the present experiments.

We may observe that n is a property of the suspension wire and λ a property of the liquid, while K may be regarded as the sum of I_0 and I_1 , where I_0 is the moment of inertia of the suspended system and I_1 represents additional inertia due to the motion of the liquid. Now inasmuch as λ depends upon the liquid, it must depend upon the viscosity η , and the density ρ . It must also depend on the scale of the apparatus, which may be represented by a length L , and on the time of vibration T .

We may write, then,

$$\lambda = f(\eta, \rho, L, T).$$

Now $\lambda/\eta L^3$ is dimensionless,

$$\therefore \frac{\lambda}{\eta L^3} = \phi\left(\frac{\eta T}{\rho L^2}\right),$$

the function on the right including all possible dimensionless combinations which can be formed from η , ρ , L , and T .

Now

$$\Lambda = \lambda T/2K,$$

$$\therefore \frac{2K\Lambda}{\eta T L^3} = \phi\left(\frac{\eta T}{\rho L^2}\right).$$

But

$$\frac{K}{I_0} = \frac{T^2}{T_0^2 (1 + \Lambda^2/4\pi^2)},$$

where T_0 is the time of vibration of the system when undamped or, to a sufficient approximation, when oscillating in air. I_0 , being the moment of inertia of the suspended system, is independent of the particular liquid.

Hence $\Lambda T/\eta (1 + \Lambda^2/4\pi^2)$ is the same function of $\eta T/\rho$ for all liquids, provided that the dimensions of the apparatus remain unchanged.

Now, in Fawsitt's experiments, K/I_0 and T/T_0 were practically unity in every case, so that if the amplitudes of vibration were small enough we should expect to find that Λ/η is a function of η/ρ , or, of course, that η/Λ is a function of η/ρ .

Figure 2 shows η/Λ plotted against η/ρ from the data obtained by Fawsitt in calibration. It will be seen that all the points are very close to a single curve; the deviations, regarded as equivalent to errors in the logarithmic decrements, being slightly less than the corresponding errors which occur when the relation used by Fawsitt is assumed to be true, namely,

$$\Lambda_{10} = C_1 \sqrt{(\eta/\rho)} + C_2 \eta + C_3 \eta \rho,$$

where Λ_{10} is the logarithmic decrement calculated to the base 10. It is assumed throughout that Λ has always been corrected by subtracting from the observed value the decrement found when the suspended system swings, without the lower disc, in air or hydrogen as the case may be, at the temperature of the main experiment.

In the present experiments, the first measurements were made with very small amplitudes, the greatest being some 7° . It was found, however, that the viscous forces were so small at these low amplitudes that the experimental errors were

somewhat serious. No change of logarithmic decrement with amplitude was actually observed under these conditions, although in the case of mercury, turbulence is liable to occur at an amplitude of about $3\frac{1}{2}^\circ$ when a disc having the same dimensions and period as that used is caused to oscillate in a very large quantity of fluid*. At first sight, then, experiments carried out with larger amplitudes would be expected to lead to a logarithmic decrement varying with amplitude, and to the possible failure of the simple method of calibration already obtained. It was, however, noticed that Fawsitt's discs were little smaller than those used in the present experiments and that his times of vibration were considerably shorter. Moreover, the amplitudes used by Fawsitt must have been large, for they were measured by means of a pointer moving over a scale divided into degrees, whereas in the present case the maximum amplitude was only about 7° , this being divided on the scale into

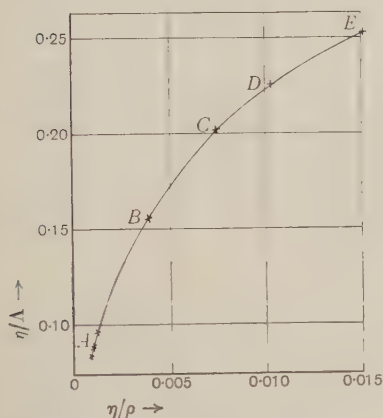


Figure 2. A mercury. B chloroform.
C benzene. D water. E ethyl alcohol.

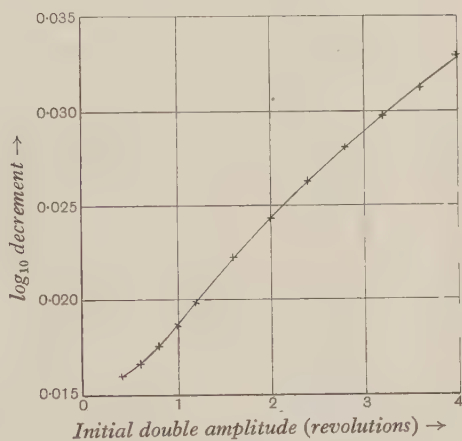


Figure 3.

500 parts. It appeared probable, then, that Fawsitt also exceeded the theoretical limits of the simple theory, and that it might be found even in the case of the higher amplitudes that we may have

$$\frac{\Lambda T}{\eta (1 + \Lambda^2/4\pi^2)} = \psi \left(\frac{\eta T}{\rho} \right)$$

or, sufficiently closely in our case,

$$\frac{\Lambda T}{\eta} = \psi \left(\frac{\eta T}{\rho} \right).$$

It was anticipated, however, that the logarithmic decrement would be a function of amplitude, and that the former would have to be calculated for a particular initial value of the latter.

Accordingly, the apparatus was modified in the manner already described, and measurements were made on mercury, chloroform, benzene, water, and isopropyl alcohol. It was found that the results depended upon the orientation of the torsion

* A. Foch and J. Bariol, *Comptes Rendus*, **193**, no. 19 (1931).

head. The effect was traced to the fact that the torsion wire was not soldered quite vertically into the centre of the disc on which the angular displacements were read. In consequence, this disc was not rotating exactly about its centre. By repeating the measurements with the torsion head rotated through 180° , and taking the mean of the two sets of measurements, this error could be eliminated.

Figure 3 shows a typical curve for water, the logarithmic decrement being plotted against the double initial amplitude; that is, against the angle between the maximum displacement to the left and the succeeding maximum displacement to the right. Subsequent calculations were based upon logarithmic decrements associated with an initial double amplitude of $1\frac{1}{2}$ revolutions, but the general nature of the results is unchanged if one, or two revolutions, be taken as fiducial values. For practical reasons it was not convenient to work with values outside these limits, the highest

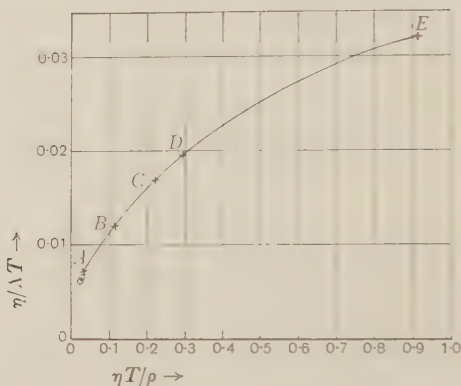


Figure 4. *A* mercury, $\rho=13.55$, $\eta=0.0156$. *B* chloroform, $\rho=1.492$, $\eta=0.00614$. *C* benzene, $\rho=0.8845$, $\eta=0.00706$. *D* water, $\rho=0.999$, $\eta=0.01054$. *E* isopropyl alcohol, $\rho=0.809$, $\eta=0.0264$.

precision being obtained from results based upon an initial double amplitude of $1\frac{1}{2}$ revolutions, which was therefore used as the fiducial amplitude.

The results first obtained for various liquids are shown in figure 4, but the lowest two points, which represent the behaviour of mercury at comparatively high temperatures, were obtained at a later stage. It will be observed that the points which were first obtained lie very close to a smooth curve.

During the course of these measurements special experiments were performed in order to ensure that no errors were liable to occur as a result of inaccurate centring of the pot, incorrect quantity of liquid, incorrect height of the disc, or inclination of the torsion head from the vertical. It was found that very little care was sufficient to reduce the errors due to any of these causes to a value much lower than that of the errors found on repeating the measurements under similar conditions. The containing vessel used had an internal diameter of 2.6 in. and was filled with liquid to a height of $1\frac{1}{2}$ in. before the immersion of the disc. The clearance between the circumference of the disc and the cylindrical surface of the pot was, therefore, 0.4 in. The middle of the disc was 0.84 in. above the bottom of the liquid.

The values of the viscosities and densities of the liquids used were obtained from the *International Critical Tables* for the particular temperatures of the experiments, except in the cases of chloroform and isopropyl alcohol. The values for these two liquids were measured in the laboratory in the usual way.

§ 4. CORRECTIONS NECESSARY AT HIGH TEMPERATURES

As the calibration curve of figure 4 appeared to be satisfactory, a series of concordant measurements was made on molten tin in an atmosphere of hydrogen. Certain corrections had to be made owing to the high temperatures at which the experiments were performed. In connexion with the corrections we shall consider again the theory of dimensions, but we shall not assume the logarithmic decrement to be independent of the amplitude. We shall assume merely that Λ depends upon η , T , ρ , L , I_0 , and θ , where L is a linear magnitude representing the size of the apparatus, I_0 is the moment of inertia of the suspended system as before, and θ is the initial amplitude, the logarithmic decrement Λ being calculated from the values of two successive double amplitudes. A knowledge of the position of equilibrium of the oscillating system is not required in this case.

Since Λ is dimensionless,

$$\Lambda = f\left(\frac{\eta T}{\rho L^2}, \frac{\rho L^5}{I_0}, \theta\right) \quad \dots\dots(2),$$

the expression on the right including all possible dimensionless quantities depending upon η , T , ρ , L , I_0 , and θ .

It will be observed that when T , L , I_0 , and θ are constant, Λ becomes a function of η/ρ and ρ , that is, an unknown function of two variables, whereas when the amplitudes are very small Λ/η is a function of η/ρ , that is, of one variable; and since η is known for every calibrating-liquid, Λ is immediately calculable when the value of Λ/η is known.

Returning to the question of corrections, we may now point out that the results of the calibration may be written approximately

$$\Lambda \propto \sqrt{(\eta T \rho)} \quad \dots\dots(3).$$

For all the liquids used, the constant of proportionality fell within the range between 0.032 and 0.038.

Comparing equations (3) and (2), we obtain

$$\Lambda \propto \frac{L^4}{I_0} \sqrt{(\eta T \rho)} \quad \dots\dots(4).$$

Three independent thermal expansions are to be considered in connexion with experiments at high temperatures, namely that of the liquid, those of the alumina disc and the containing vessel, and that of the steel inertia disc. The preliminary experiments showed that the effect of the expansion of the liquid may be ignored. The same is true of the lowering of the disc with respect to the pot, which occurs at high temperatures owing to the difference in the rates of expansion of steel and

silica. The effects of the expansions of the two discs must, however, be allowed for in accordance with equation (4)*.

Since most of the inertia of the system is due to the steel disc, a knowledge of the coefficient of expansion of steel is sufficient for the calculation of the change of I_0 . This value can also be obtained by comparing the times of vibration of the apparatus in an atmosphere of hydrogen at high and at low temperatures, for, owing to the water cooling, the elasticity of the suspension wire is substantially constant.

These corrections are actually very small, since the effects of the expansions of the alumina and steel discs have opposite effects on the value of Λ , resulting in a zero correction at the melting point of tin and a correction of slightly less than 1 per cent of Λ , or rather less than 2 per cent of η , at 800° C. At still higher temperatures the correction grows rapidly. The principles involved have been explained in some detail because experiments might be made by other workers at considerably higher temperatures, and the explanation given by Fawsitt appears to be incorrect. It may be mentioned in passing that the expansion of all forms of calcined alumina is substantially the same as that of fused alumina so long as the heating, in the former case, is insufficient to produce a permanent contraction†. The discs used in our experiments were made of pure alumina by the process of slip casting and were fired to 1530° C. The stems were made separately, the ends being turned in the lathe. The lower end of the stem made a tight tapered fit in the disc, and the upper end was fixed in the steel disc with the aid of a refractory cement, the operation being conducted with great care in the lathe.

As was previously mentioned, the logarithmic decrements require correction for the influence of the resistance of the gas in the apparatus, and the imperfect elasticity of the suspension wire. This correction depends very considerably on temperature; the logarithmic decrement of the system in hydrogen, without the alumina disc, varies from 0.002 at 16° C. to 0.0035 at 800° C. The change of this quantity with temperature was not considered by Fawsitt. In the present experiments this correction amounts, in the case of tin at a temperature of 800° C., to 7 per cent of the logarithmic decrement or 14 per cent of the apparent value of the viscosity.

§ 5. RESULTS OF MEASUREMENTS ON TIN, AND COMPARISON WITH THOSE OF OTHER INVESTIGATORS

The logarithmic decrements in the case of tin for a fiducial double-amplitude of $1\frac{1}{2}$ revolutions are shown in figure 5. On calculation of the viscosity values with the aid of figure 4 and with values of ρ obtained from the *International Critical Tables*,

* The expansion of the pot has no appreciable effect on the value of Λ , the effect of a change of L being really ascribable to the change in dimensions of the alumina disc alone. This remark applies only to the conditions of our experiments. For example, if we were dealing with liquids of extremely high viscosity we should find Λ proportional to $L^3 \eta T I_0$, and in this case the effect of a change of L would not be ascribable to the change in dimensions of the disc alone, but would include the effect of the expansion of the pot and the liquid. As the liquid would expand at a different rate from that of the disc and pot in such a case, special experiments would be needed to determine the correction.

† George E. Merritt, *Trans. Amer. Electrochem. Soc.* **50**, 165 (1926); H. Forestier, *Annales de Chimie*, **9**, 316 (1928).

it was found that the temperature coefficient of viscosity was much less than that found by Sauerwald and Töpler*, the two curves which express the relation of viscosity to temperature crossing at about the middle of the range. A careful consideration of the work of Sauerwald and Töpler, who used the capillary-tube method, failed to disclose any probable source of serious error, the accuracy of the experiments being estimated by these authors as within about 1 per cent.

A consideration of the viscosities and densities of the liquids used in calibration, suggested that the proximity of the various points to the calibration curve of figure 4 might be fortuitous, and that divergences might be found in the case of other liquids since, as had been explained, there is no strong reason for the belief that the representative points should lie on a single curve in the case of oscillations of large amplitude. In order to test this supposition, liquids of high density with various viscosities are required. The practical choice is restricted to mercury at high temperatures if we leave out of account other metals, such as tin and lead, the

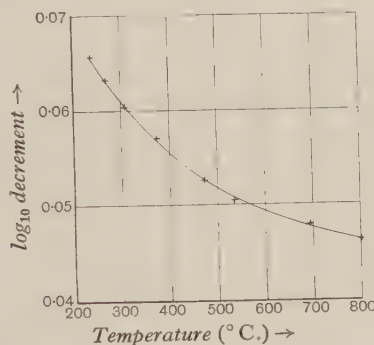


Figure 5. Results for tin.

viscosities of which cannot be regarded as established with a high degree of certainty. Experiments were therefore carried out on mercury, beginning at room temperatures. Difficulty in making consistent measurements was initially experienced owing to slight contamination of the disc with the tin previously used. Less than one part in a million of impurity in mercury results in the production of a surface layer of remarkable mechanical strength, which seriously interferes with the measurements. It was mainly owing to the disturbing influence of surface effects in the case of mercury that the earlier experiments at very small amplitudes had to be abandoned. Fawsitt, who melted his tin in air, had to cover the surface with a flux. If we assume the correctness of Sauerwald's values, Fawsitt obtained a value some 30 per cent too high for the viscosity of tin at a low temperature. He recognized, however, the probability of a considerable error of this nature. In the present experiments it was found that the very small amount of contamination of the disc could be removed by repeated washing with pure mercury, after which the original calibration was repeated closely several times. These experiments were carried out in air, both inside and outside the furnace, proper correction being made in each case for the part of

* F. Sauerwald and K. Töpler, *Z. f. Anorganische und Allgemeine Chemie*, **157**, 117 (1926).

the decrement due to subsidiary resistances. On raising the temperature of the mercury it was found that surface contamination occurred, and finally, as a result of an accident, the disc was broken. A new disc gave concordant results at room temperatures, the decrement being about 10 per cent higher than those measured with the old disc. It was assumed that this ratio is independent of viscosity, and concordant measurements were then made at higher temperatures in an atmosphere of hydrogen, which suppressed the contamination of the surface.

The results obtained are represented in figure 4 by the lowest two points, and, as was to be anticipated, they do not lie strictly on the original calibration curve.

It was also found that an equation of the kind used by Fawsitt gave results similar to those calculated from the calibration curve, and therefore inconsistent with Sauerwald's values for tin. Agreement may be obtained by the use of an equation of the form

$$\Lambda = A\sqrt{(\eta T\rho)} + B\eta T\rho + C\eta T + D\rho,$$

but even in this case the best values of the constants cannot be determined sufficiently accurately without the use of some metal having a lower density than that of mercury. It follows that this method of measurement must always be based upon calibration performed on metals having hydrodynamical properties fairly close to those of the metal under investigation, unless it be possible to work at very low amplitudes. At very high temperatures, however, the logarithmic-decrement method appears to be the only practicable one, and the considerations put forward may be of assistance to anyone undertaking such measurements.

Although, as we have seen, the general determination of Λ as a function of η , T , and ρ , is a matter of great difficulty, the relations appear to be simpler if we restrict our enquiries to the case of liquids of high density. Thus, the results of the measurements on tin and mercury may be expressed by the simple relation

$$\Lambda = 0.0101 + 0.0278\sqrt{(\eta T\rho)},$$

the greatest deviation being less than 1 per cent of the value of Λ^* . It is interesting to note that Thielmann and Wimmer† calibrated a somewhat similar apparatus, using for the purpose mercury, tin, and bismuth, and assumed that

$$\Lambda = x_1(\eta\rho)^{\frac{1}{2}} + x_2\eta\rho + x_3(\eta\rho)^{\frac{3}{2}},$$

where x_1 , x_2 , and x_3 are constants. Details are not available, however, of the values of these constants, nor of the amplitudes and times of vibration employed. Great difficulties were met by these authors in connexion with oxidation at the surface of the metal, and it is probable that the present experiments on tin are the first in which this difficulty has been overcome at high temperatures. These experiments have also permitted an extension of Sauerwald's data on tin. Figure 6 shows the values of Λ , plotted against the values of $\eta^{\frac{1}{2}}$ obtained from Sauerwald's smoothed results. By extrapolating this curve for a short distance at each end we may calculate values of η , with the aid of our measurements of Λ , for temperatures some 60° lower

* The formula is, of course, based on Sauerwald's values for the viscosity of tin between 300° C. and 750° C.

† *Stahl und Eisen*, 47, 389 (1927).

and 50° higher than the range covered by Sauerwald. From these calculations, and Sauerwald's smoothed values, the following table has been constructed.

Temperature ($^{\circ}$ C.)	η (poises)	Temperature ($^{\circ}$ C.)	η (poises)	Temperature ($^{\circ}$ C.)	η (poises)
240	0.0191	420	0.0133	620	0.01025
260	0.0182	440	0.0129	640	0.01005
280	0.0174	460	0.0125	660	0.00985
300	0.0167	480	0.0122	680	0.00965
320	0.0160	500	0.0118	700	0.00945
340	0.0154	520	0.0115	720	0.0093
360	0.0148	540	0.01125	740	0.00915
380	0.0143	560	0.0110	760	0.0090
400	0.0138	580	0.0107	780	0.00885
—	—	600	0.0105	800	0.0087

No discontinuity of viscosity as a function of temperature was observed down to a temperature of 238° C., six degrees above the solidification point. Fawsitt approached this point so closely that partial solidification of the melt actually occurred, but no discontinuity was observed. We may therefore assume continuity down to the freezing point of the tin. The viscosity at this temperature (232° C.) is 0.0195 poise.

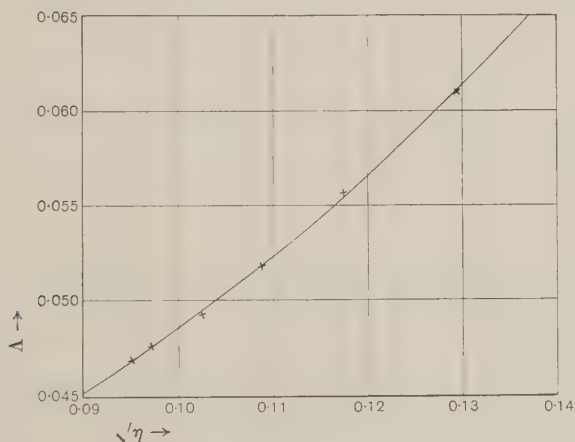


Figure 6. Results for tin.

It has been assumed that the experiments of Sauerwald and Töpler are substantially correct, this assumption being based upon a critical study of their method. Measurements have also been made by Plüss* by a similar method, but with rather less refinement. At a temperature of 280° C. Plüss found a value for η about 3 per cent lower than that subsequently found by Sauerwald and Töpler. At a temperature of 390° C. the discrepancy amounts to rather more than 6 per cent, the variation of viscosity with temperature found by Sauerwald and Töpler being definitely less than that found by Plüss. No other reliable measurements appear to have been made.

* *Z. f. anorganische und allgemeine Chemie*, **93**, 1 (1915).

The most recent measurements of the fluidities of a large number of molten metals and alloys have been made by Losana*. The values are said to be relative to the fluidity of tin at a temperature of 300° C. They were determined for the most part with the aid of an oscillating cylinder, no precautions being taken against oxidation other than covering the crucible with a sheet of asbestos. The method of calculating even relative values is erroneous, and a comparison of the results for mercury and tin reveals serious inconsistency if Sauerwald's values are approximately correct. Since, however, the effect of oxidation enters into foundry practice, Losana's results correspond in some degree with that practice, to the limited extent to which considerations of fluidity have a determining influence in connexion with the ease of production of castings.

§ 6. CONCLUSION

The general conclusion emerges, from the present work, that the oscillating-disc method of measuring the viscosities of molten metals is capable of yielding satisfactory results if proper attention be given to the theoretical principles involved, and if the calibration be based on metals having densities and viscosities of known values, which should not be very different from those of the metals under investigation. For this purpose it is desirable to check, by the capillary-tube method, the values obtained by Sauerwald and his co-workers, and perhaps, to extend them. The oscillating-disc method may then be used for cases to which the capillary-tube method is inapplicable, but in the case of the former method it is essential that thorough precautions should be taken to avoid errors due to contamination of the surface of the melt.

DISCUSSION

Mr J. H. AWBERY. The figures in the table are interesting, even though I believe they are only Sauerwald's values extrapolated, and not deductions from the author's experiments.

If $\log \eta$ is plotted against $1/\theta$, where η is the viscosity and θ the absolute temperature, the points lie moderately well on a straight line, in accordance with the formula given recently by Andrade. It has been suggested by R. O. Herzog and H. C. Kudar† that the slope b of the line is connected with the latent heat of fusion of the substance concerned. According to their theory, the latent heat of tin comes out at 12.1 gm.-cal. gm., which may be compared with the calorimetrically determined value of 14.6‡ found by Dr Griffiths and the speaker.

I have said that the author's table only consists of Sauerwald's values extrapolated. The method is a little more subtle than if he had merely plotted η against θ and extrapolated the curve with a spline. Suppose he had adopted the following alternative method: Draw, as curve A , any one-valued continuous function of θ , which need not be defined by any analytic expression whatever, but is to be defined

* Luigi Losana, *Il Notizario Chimico-Industriale*, **2**, 1, 63, 121 (1927).

† *Z.f. Phys.* **80**, 217 (1933).

‡ *Proc. Phys. Soc.* **38**, 378 (1926).

for a range of values of θ greater at each end than the range of values covered by Sauerwald's experiments. As curve *B*, plot Sauerwald's values of η against this function $f(\theta)$. Curve *B* will only exist over the range covered by Sauerwald. Now by extending curve *B* we can draw up a table of values of η against $f(\theta)$ over a wider range, and this is an extrapolation of Sauerwald's values only. Once this is done, the table is converted easily to a table of η against θ , by the aid of curve *A*. The extrapolation makes no use of the properties of the function f , except that the latter is taken to be continuous.

This method is the one adopted by the author, who takes $f(\theta)$ as equal to Λ , the experimental logarithmic decrement, for which experiment alone can and does answer the question as to continuity.

Is it too late to ask him to give his experimental results? If Sauerwald's work should be repeated and not confirmed, the necessary modifications in the author's table could not be made without this information. Moreover, if it should ever prove possible to provide a calibration curve, of the nature of figure 4, applicable to the conditions of these experiments, the original data would be of great value.

MR A. J. LEWIS. In searching for a method to extend the knowledge of the viscosity of tin, I decided against the logarithmic-decrement method for various reasons: (a) the effects of slight contamination of the surface by oxide and other impurities seem to be almost as great as in the capillary method, and the exposed area is greater. In particular, imperfections near the suspension seem to have an abnormal effect; (b) because results depend on the elastic properties of a suspension at different temperatures; (c) because the theory is in a highly complicated and rather uncertain state. The method cannot be used for absolute determinations, and relative measurements cannot be made with such certainty as by the capillary method. I have therefore adopted the capillary method and am at present engaged in measuring the viscosity of tin by it. These objections have been met in a masterly way by the author of the present paper. In connexion with (a) I would like to ask if greater difficulty was experienced in overcoming oxidation troubles at temperatures near the freezing point than at higher temperatures. Sauerwald and Töpler were unable to obtain satisfactory results below 300° C. on account of this increased difficulty.

AUTHOR'S reply. In reply to Mr Awbery: I am very interested to hear that there may be a connexion between viscosity, temperature, and latent heat. The question raised with regard to the extension of Sauerwald's values is even more subtle than Mr Awbery suggests. His explanation of my procedure, whilst mathematically correct, is physically incomplete. The logarithmic decrement Λ is essentially a function of the viscosity η and is only incidentally a function of temperature. (The density ρ and the time of vibration T have each an influence on Λ but their variations were very small, and both ρ and T were continuous functions of η . This is obvious in the case of ρ . The explanation in the case of T follows from the fact that the variations of T were due to the variations in the dimensions of the discs as a result of temperature changes, and it turns out that the viscosity of tin is a

continuous function of temperature.) The relation between Λ and η was established by determining Λ at a number of different temperatures, and obtaining the corresponding values of η from Sauerwald's work. The next step was to extrapolate the curve connecting Λ with $\sqrt{\eta}$. The relationship between these quantities has a hydrodynamic basis which, except for the small effects due to variations of ρ and T , is independent of the (viscosity, temperature) curve of tin. Furthermore, it is reasonable to suppose that the former curve is continuous, for the effects of discontinuities due to the turbulent flow in the liquid are smoothed because each oscillation of the system involves a range of velocities from zero to a maximum value. For the same reason the (logarithmic-decrement, amplitude) curve is continuous, as may be seen from figure 3. Finally, it may be noted that the procedure which I adopted would probably have given correct results even had there been a discontinuity in the (viscosity, temperature) curve of tin in the neighbourhood of the melting point. It is evident, therefore, that the method involves more than the mere extrapolation of Sauerwald's curve. Considerations of space hardly justify the publication of all the experimental results, which would probably be considerably modified by comparatively small changes in the experimental arrangements.

In reply to Mr Lewis I may say that no difficulties were encountered in connexion with the measurements on tin at any temperature. Indeed, these measurements were more concordant than those made for the purpose of calibration. I am very glad that Mr Lewis is checking Sauerwald's results, as circumstances prevent my undertaking similar work.

TWO SIMPLE METHODS OF ABSOLUTE MEASUREMENT OF ELECTRICAL RESISTANCE IN TERMS OF INDUCTANCE AND FREQUENCY

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AND

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ABSTRACT. In the first method a sinusoidal alternating current of some 15 mA. derived from a valve oscillator and of frequency equal to that of a König tuning-fork is allowed to induce an equal current in a secondary circuit. The equality of amplitude of the primary and secondary currents is judged with the aid of a Westinghouse instrument rectifier. The resistance of the secondary circuit is given by the expression

$$S = 2\pi n \sqrt{(M^2 - N^2)},$$

where n is the frequency, N the self-inductance of the secondary and M the mutual inductance between the primary and secondary. With standard forks of frequencies 256, 320, 384 and 512, resistances have been measured ranging from 16Ω to 67Ω .

In the second method equal primary and secondary currents of known frequency are also produced and are further adjusted to be in quadrature. A simple arrangement is thereby derived which enables Campbell's two-phase alternating-current method of measuring resistance to be carried out in the laboratory.

In both methods a visibly beating circuit is employed which enables the frequency of the current used to be tuned easily, with precision, to that of a valve-maintained fork. This beating circuit is also of value in checking the relative accuracy of forks whose frequencies are very approximately in simple ratio to one another.

§ 1. PRINCIPLE OF THE FIRST METHOD

A PRIMARY circuit consists of a valve oscillator, resistance R , relatively large inductance L and neutralizing capacitance K . A secondary circuit of small self-inductance N and having a mutual inductance M , greater than N , with the primary circuit, has a total resistance S . The amplitudes of the primary and secondary currents are adjusted to equality by varying S or M , while the frequency n of the currents is adjusted to that of a valve-maintained König tuning-fork so that the beats, rendered visible, are of the order of 1 a minute.

Under such conditions the resistance of the secondary circuit is given by the relationship

$$S = 2\pi n \sqrt{(M^2 - N^2)} \quad \dots\dots(1).$$

R
 L, K
 N, M
 S
 n

This expression readily follows* from the well-known equations of a primary and secondary circuit, namely

$$\left(L - \frac{1}{\kappa\omega^2}\right) \frac{di_1}{dt} + M \frac{di_2}{dt} + Ri_1 = Ee^{j\omega t} \quad \dots\dots(2a),$$

$$M \frac{di_1}{dt} + N \frac{di_2}{dt} + Si_2 = 0 \quad \dots\dots(2b),$$

where i_1, i_2 are the respective instantaneous values of the primary and secondary currents when a sinusoidal alternating e.m.f. of pulsance ω equal to $2\pi n$ is applied to the primary circuit. For these equations give, for the ratio of the currents,

$$i_2/i_1 = -Mj\omega/(S + Nj\omega) \quad \dots\dots(3).$$

Thus the ratio of the secondary and primary current-amplitudes is in general $M\omega/\sqrt{(S^2 + N^2\omega^2)}$, and equation (1) results when these amplitudes are equal.

§ 2. THE EXPERIMENTAL ARRANGEMENT FOR METHOD I

The primary circuit. A simple valve oscillator V , figure 1, was allowed to give a current of some 15 mA. through capacitance K , a variable self-inductance L_1 ,

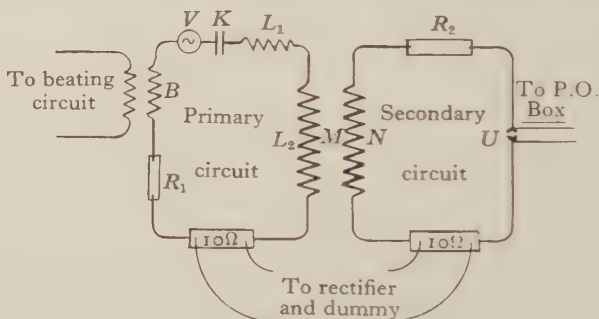


Figure 1. Simple circuit for absolute measurement of resistance.

a coil or coils of self-inductance L_2 linked with the secondary circuit, a coil B supplying energy to the beating circuit described below, a resistance box R_1 and a standard 10-ohm non-inductive resistance. The primary of a Campbell mutual inductometer could at any time be switched into the circuit.

The anode circuit of the oscillating valve (Mazda P 220) had adjustable capacitance including a variable 0.001- μ F. condenser. The inductance L_2 consisted of one or two twin coils of self-inductance 0.15 H., resistance 15 Ω , turns 500 and mean diameter 35 cm. The total effective inductance of the circuit was approximately neutralized, for the frequency used, by the capacitance K .

The secondary circuit. The secondary circuit included a coil N of 67 turns of s.w.g. 18 insulated copper wire about 31 cm. in diameter and of self-inductance 3242 μ H. The coil had a maximum mutual inductance of 10500 μ H. with either of the

* Cf. S. G. Starling, *Magnetism and Electricity*, pp. 359-61 (4th edition); A. Gray, *Absolute Measurements in Magnetism and Electricity*, pp. 251, 252; J. H. Jeans, *Electricity and Magnetism*, pp. 465, 466 (4th edition).

twin coils L_2 of the primary circuit. The rest of the circuit consisted of a non-inductive resistance box R_2 adjustable to 0.01Ω , a standard non-inductive $10\text{-}\Omega$ resistance similar to that in the primary circuit, and a plug key U which could be either closed to complete the secondary circuit or opened to permit connection with an accurate Post Office box, so that the total resistance S of the circuit could be measured. At any time the secondary of the Campbell mutual inductometer in series with a telephone could be included in the circuit.

The equal-amplitude tester. The $10\text{-}\Omega$ coils in the primary and secondary circuits were those of an accurate non-inductive ratio box and were connected, via potential leads, to a mercury rock-over key enabling either to be shunted at will by a circuit consisting of 500Ω , a full-wave instrument-type Westinghouse metal rectifier (specified as 4-1-1, 50 mA. Inst. unit) and a unipivot $0\text{--}120$ d.-c. millivoltmeter. Equality of amplitude was judged by identity of deflection of the millivoltmeter as viewed through a microscope with an eye-piece scale on very quickly rocking over the switch, such identity of deflection having been carefully verified when the $10\text{-}\Omega$ coils were in series in the same circuit.

As the Westinghouse shunt circuit is not of infinite resistance, and as the primary and secondary currents are interdependent and have circuits of unequal impedance, special precautions have to be taken in accurately judging identity of current-amplitude. For the actual operation of the rock-over will very slightly modify the currents, and this effect, though small, is not symmetrical. Accordingly a dummy circuit of $1650\text{-}\Omega$ resistance was prepared and was always switched on to the primary 10Ω when the secondary 10Ω was on the Westinghouse circuit, and likewise always rocked on to the secondary 10Ω when the primary 10Ω was on the Westinghouse circuit. This dummy resistance was that of the Westinghouse circuit for the order of the deflection used and was such that the resistance of the secondary circuit, even when small, was the same whether the 10Ω in this circuit was shunted by the dummy or by the Westinghouse arrangement. This equality of resistance was judged by means of a P.-O.-box test with such a direct current, in either direction, as would produce the standard millivoltmeter deflection when the battery key was depressed.

Though this compensating device is most satisfactory it is no longer necessary if the voltages tapped off the $10\text{-}\Omega$ coils are switched in turn to the filament and grid of an amplifying valve, the anode current of which is passed through a transformer and thence to the Westinghouse circuit with added resistance. Rectifier M.B.S. 10 is now sufficiently sensitive.

The visible-beater. The output transformer from a valve-maintained tuning-fork was connected to a coil P_1 , figure 2, forming an adjustable mutual inductance with a secondary S_1 . Likewise the output from the coil B , figure 1, in the valve oscillator primary circuit was led to a coil P_2 , figure 2, forming an adjustable mutual inductance with the secondary S_2 . The secondaries S_1 , S_2 were connected in series through a resistance box R , having a telephone T across it, to a Westinghouse metal rectifier W and a unipivot $0\text{--}120$ d.-c. millivoltmeter MV . If desired a push-pull wireless transformer having two equal primaries and a common secondary may be substi-

tuted for the coils P_1 , P_2 , S_1 , S_2 , provided the inputs into the primaries are under control.

If the frequencies of the fork and valve-oscillator current are sufficiently near one another, beats may be heard in the telephone T and seen by the oscillations of the millivoltmeter pointer and so may be counted by both ear and eye. As the variable condenser on the oscillator is turned to bring the frequencies more closely into unison the beats become too slow to be recognized by ear, but the pointer oscillations increase in amplitude and are easily timed by eye. If the steady millivoltmeter deflections, due to each source separately, are made approximately equal at a quarter-scale reading, elegant full-scale swings of the pointer of many seconds' period may be produced when both sources are in operation, and the final tuning to unison is remarkably exact.

If both input circuits are derived from valve-maintained forks whose frequencies are very approximately in simple ratio to one another, beats between the common

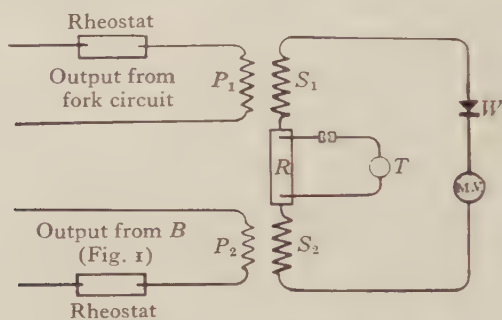


Figure 2. The visibly beating circuit.

harmonic components of the currents in the driving circuits, though of small amplitude, are readily seen and counted. Thus a König C 256 fork gave rise to beats of period 3.7 sec. when used in conjunction with a König E fork of frequency $320 + x$. These beats are between the current harmonics of frequencies 5×256 and $4 \times (320 + x)$ and were suppressed by a very minute load upon the E fork. A rapid and accurate check on the relative frequencies of the forks used can thus be easily effected, and data are given in table 5 below.

§ 3. EXPERIMENTAL TESTS (METHOD 1)

In performing an experiment the capacitance K , figure 1, was adjusted so as to neutralize approximately the total inductance of the primary circuit for the frequency used, while the anode condenser of the oscillator was chosen to produce visible beating with the standard valve-maintained fork, these adjustments being successive.

The resistance of the secondary circuit was set to produce an induced current approximately equal to the primary current, the final exact adjustment being made after tuning the oscillator to beat with the fork not more than once a minute. Any slight drift of frequency was easily corrected by a slight turn of the anode $0.001\text{-}\mu\text{F}$. condenser.

As soon as currents of equal amplitude, as judged by several rock-overs, had been obtained, the oscillator was switched off and the resistance of the secondary circuit was measured on a reliable Post Office box after removal of the plug key U , the resistance of the leads (as taken when the plug key was inserted) having been adjusted previously to an exact number of hundredths of an ohm. Whether the secondary 10Ω was shunted by the dummy or by the Westinghouse circuit the value of S thus obtained was in all cases the same to the nearest 0.01Ω .

The mutual inductance M between the primary and secondary was then measured with a Campbell mutual inductometer, the primary of which was switched into the primary circuit while the secondary and telephone were inserted in the secondary circuit. The usual impurity device was included and the frequency was maintained, by adjusting capacitance, at approximately that of the fork.

The self-inductance N of the secondary circuit is of smaller importance than M and was practically constant throughout the experiments. It was measured twice with the Heaviside-Campbell equal ratio bridge and found to be $3242\mu\text{H}$.

Variation of M for further tests was obtained by using one or both of the twin coils L_2 and by separating L_2 and N . As the range of the inductometer was limited to $11,100\mu\text{H}$. it was necessary when working above this range to add to it, at sufficient distance of separation, a $10,000\mu\text{H}$. standard of mutual inductance which could readily be cross-checked against the inductometer.

The results in tables 1 to 5 form a continuous series obtained when the mains were used with an eliminator as a source of high tension for the oscillator. Even in spite of slight fluctuations due to the d.-c. mains the equal-amplitude tester was very sensitive to changes of secondary resistance, which affect the primary and secondary currents in opposite directions. A change of $\pm 0.02\Omega$ clearly upset the equilibrium when the secondary resistance was some 25Ω , and a change of $\pm 0.05\Omega$ did so when the value of the secondary was 67Ω . We found later that if a high-tension battery was substituted for the mains and eliminator perfect quiescence was obtained, allowing a higher-power microscope to be used and aiding the ease and certainty of the equal-amplitude setting. Under such circumstances a secondary resistance of 32Ω could be set by the tester to within $\pm 0.01\Omega$.

Tables 1, 2, 3 and 4 give data for the four frequencies used. S is calculated from the relationship $S = 2\pi n \sqrt{(M^2 - N^2)}$ after M and N have been expressed in centimetres by multiplying the readings in microhenries by 10^3 . Table 5 gives the

Table 1. Results when $n = 512$, $N = 3242\mu\text{H}$.

M (μH .)	$S \times 10^{-9}$ (c.g.s.u.)	Resistance by bridge (Ω)
21090	67.04	67.09
18629	59.02	59.07
16626	52.46	52.50
10557	32.32	32.31
10510	32.16	32.14
8067	23.76	23.73
6025	16.34	16.30 ₈

Table 2. Results when $n = 384$, $N = 3242 \mu\text{H}$.

$M (\mu\text{H.})$	$S \times 10^{-9}$ (c.g.s.u.)	Resistance by bridge (Ω)
21087	50.27	50.21
18790	44.66	44.66 ₅
16695	39.51	39.49 ₅
13608	31.89	31.87
10578	24.29	24.29
8085	17.87	17.88

Table 3. Results when $n = 320$, $N = 3242 \mu\text{H}$.

$M (\mu\text{H.})$	$S \times 10^{-9}$ (c.g.s.u.)	Resistance by bridge (Ω)
10553	20.19	20.25
21097	41.91	41.87
18757	37.15	37.17
16718	32.97 ₅	32.96 ₅
13703	26.77	26.79

Table 4. Results when $n = 256$, $N = 3242 \mu\text{H}$.

$M (\mu\text{H.})$	$S \times 10^{-9}$ (c.g.s.u.)	Resistance by bridge (Ω)
21067	33.48	33.51
18651	29.54	29.60
16634	26.24	26.26
13615	21.27	21.29
10746	16.48	16.50
10746*	16.48	16.47

* A second König fork, 256 B, was used in this experiment.

Table 5. Beats produced by valve-maintained tuning-forks

Beating* forks	Interval	Frequency of common octave	Time occu- pied by 10 beats in seconds	Corrected frequency of second fork
256 & 320	major third	1280	37	320.07
256 & 384	fifth	768	50.5	384.10
256 & 512	octave	512	88	512.11
256 & 256 B	unison	256	123	256.08

* The second fork in all cases required load for perfect harmony.

beats between the 256 fork and the others: the corrected value of the higher fork is relative only, the 256 fork being assumed to be correct. Such corrections have been neglected in the calculation of S .

§ 4. METHOD 2: A SIMPLE FORM OF CAMPBELL'S TWO-PHASE ALTERNATING CURRENT METHOD OF MEASURING RESISTANCE

If the arrangement shown in figure 1 be modified so as to take the form shown in figure 3 we have a circuit which is of value in teaching Campbell's method* of determining the ohm, and experiments may be carried out with a current of 15 mA. derived from a simple valve oscillator.

The primary circuit now includes the primary P' of a variable mutual inductance, preferably that of a Campbell mutual inductometer. The secondary circuit has two additions, viz. the resistance R whose magnitude is required, with potential leads, and the phase-adjuster consisting of a capacitance K' in parallel with a variable non-inductive resistance R_3 which permits of fine adjustment. The object of this multiple-arc arrangement is to neutralize the small self-inductance N of the secondary circuit so that the induced current shall be in quadrature with the primary current as well as ultimately equal to it in amplitude. Such compensation is attained when

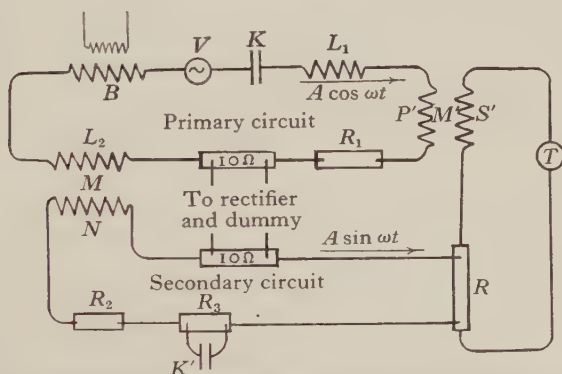


Figure 3. Simple form of Campbell two-phase alternating current method of measuring resistance.

$N = R_3^2 K'$ approximately and is almost independent of frequency, which only slightly influences the equivalent resistance. As the inductance-neutralizer introduces effective resistance into the circuit, and as the secondary current is limited when equal to the primary by the relationship

$$S = 2\pi nM$$

(N being now zero), it is well to use as a standard of frequency a valve-maintained fork of frequency not less than 512, and to set M at its largest value (in our case 21,000 μ H.). The resistance R is connected to the telephone T and the secondary S' of the mutual inductometer.

If by adjusting the mutual inductance M' silence can be obtained in the telephone when the primary and secondary currents are in quadrature as well as equal in amplitude, we have Campbell's relationship

$$R = 2\pi nM' \quad \dots\dots(4).$$

* A. Campbell, *Proc. R. S.* **81**, 450 (1908); **87**, 398 (1912). For a brief account see the *Dictionary of Applied Physics*, **2**, 224, 426.

In performing a first experiment the capacitance K in the primary circuit and the oscillator condenser were adjusted successively, as in § 3 above, to neutralize approximately the primary inductance and to produce visible beats with a valve-maintained König fork of frequency 512. The resistance R was one of the 10- Ω ratio arms of a Post Office box. K' was about $2\mu\text{F}$. and the resistance R_3 was adjusted until, irrespective of equality of amplitude of the two currents, a reasonably sharp inductometer balance, as judged by approach to silence in the telephone T , was obtained. This occurred when R_3 was about 40Ω and it showed the close approach to perfect quadrature, the secondary circuit being approximately non-inductive. The primary and secondary currents were now adjusted to equality with the box R_2 , as judged by the equal-amplitude tester, the frequency was controlled to obtain visible beats not exceeding one a minute, and R_3 was slightly adjusted for sharpness of inductometer-telephone balance. The adjustments were successive. A sharp reading for M' was thus obtained without the slightest difficulty, and a zero reading, equally sharp, was taken similarly with the 10- Ω plug of R inserted.

By making K' about $2.3\mu\text{F}$., R_3 was reduced to some 38Ω , permitting R to be increased to 20Ω while leaving sufficient surplus secondary resistance to allow of equal-amplitude adjustment with the box R_2 . Table 6 shows the readings obtained.

Table 6. Determination of resistance by Campbell's method

$$n = 512, R = 2\pi nM'$$

Nominal value of R	K' (μF .) approx.	R_3 (Ω) approx.	M' (μH .)	$R \times 10^{-9}$ (c.g.s.u.)	Resistance as measured with bridge (Ω)
zero (plugs inserted)	2	40	zero (by zero adjuster)	—	zero (lead reading taken)
10 Ω (left arm)	2	40	3101	9.976	9.98
10 Ω (right arm)	2	40	3102	9.976	9.98
20 Ω (both arms)	2.3	38	6208	19.97	19.96

§ 5. CONCLUDING REMARKS

The experiments described in this paper may be simplified and readily performed by advanced students. Inexpensive condensers may be used for capacitance in both methods. If no inductometer is available, the fundamental relationships involved in the methods, viz. those of equations (1) and (4), may be tested by resorting to the Owen and Carey Foster bridges for the measurements of self and mutual inductance respectively, though the absolute character of the methods is thereby sacrificed.

By virtue of the high inductance of the primary circuits, which ensures that the currents are minute until neutralizing capacitance for the fundamental frequency is introduced, error due to the presence of harmonics appears to be very small and inductometer balances are sharp.

§ 6. ACKNOWLEDGMENTS

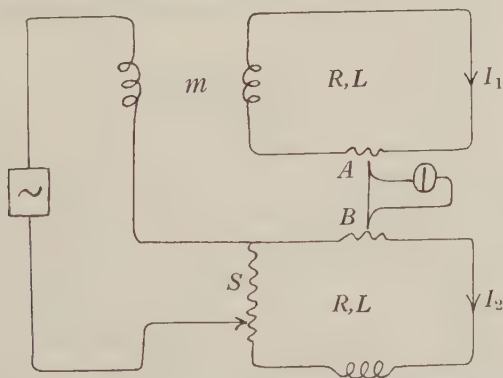
We express our gratitude to Prof. A. Griffiths who has generously provided us with apparatus and to Dr D. Owen, of the Sir John Cass Technical Institute, for the loan of a variable self-inductance. We thank Mr W. Wilson, Mr S. Baker and Mr R. Edgerton of the Physics Department, Birkbeck College, for suggestions and for assistance in our measurements.

DISCUSSION

Dr D. OWEN. The authors' first method utilizes ingeniously the fact that in the a.-c. transformer there is a simple relation between the resistance of the secondary, the mutual inductance, the self-inductance of the secondary, and the frequency, if the primary and secondary currents are exactly equal. From this relation the resistance of the whole of the secondary circuit may be calculated in absolute measure. It must be borne in mind that the effective a.-c. resistance of a coil is not equal to its d.-c. value, but always in excess of it, to an extent increasing with the frequency. It would have been of interest if results for the same circuit at various frequencies could have been recorded. The second method furnishes a simple means of carrying out A. Campbell's a.-c. determination of absolute resistance, which may with advantage be included in the laboratory course of the advanced physics student.

Mr A. CAMPBELL. The authors' second method is quite suitable for an ordinary laboratory and the results show that it can give good accuracy. Some time ago I introduced a somewhat similar system as a phase-splitter for a.-c. potentiometers*. It is rather simpler in detail than that of the authors, but not so self-contained for students' use.

In the accompanying figure the two loops have equal total resistance R and self-inductance L , being set by preliminary tests. The currents I_1 and I_2 will thus



be always in quadrature. By means of differential thermo-junctions and heaters A and B , by altering either S or m , we can get

$$I_2 = I_1.$$

* British Patent Specification No. 342,441.

Then

$$S = \omega m = 2\pi n m,$$

which determines the resistance S in terms of m and n . With ordinary apparatus I have obtained accuracy to about 1 part in 2000.

I have suggested the system to Dr Hartshorn as an alternative to my M - R method, by which the National Physical Laboratory has recently made a determination of the ohm. It is sufficiently sensitive and requires very little apparatus, but it has one weak point—the accuracy is lowered by the presence of harmonics, for balance is obtained by making the effective (r.m.s.) values of I_1 and I_2 equal, and not, as in the M - R method, by use of a selective vibration galvanometer.

AUTHORS' reply. In reply to Dr D. Owen: We hope to carry out shortly further tests on the absolute measurement of resistance by a yet more simple a.-c. method. We shall certainly keep his suggestion in mind and measure the same resistance under different frequencies.

We are very interested to learn that Mr Albert Campbell has used a simple device in which two currents, always in quadrature, are adjusted to equality to enable a resistance to be measured absolutely in terms of a mutual inductance and a frequency. The circuit of figure 3 is designed for teaching purposes to resemble the original arrangement as closely as possible and it is perhaps an advantage that the student has to perform the adjustment for quadrature carefully to obtain sharpness of balance.

THE DEMONSTRATION OF EDDY CURRENTS IN CONDUCTORS OF VARIOUS SHAPES

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*Received March 13, 1933. Read and demonstrated, in the absence of the author,
by Prof. P. W. Burbidge, May 19, 1933*

ABSTRACT. In this paper a method is described whereby it is possible to demonstrate visually the existence of eddy or Foucault currents in masses of conducting material, and the way in which the flow of the currents may be distorted or baffled by suitable slots or laminations. The experiment is very easy to set up, and would make a good conversazione experiment.

IN the teaching of electromagnetic induction, demonstrations of the existence of eddy currents are usually of an indirect character, involving the resistance to motion of a mass of metal in a magnetic field or the rise in temperature of the metal. It is thought that the following method enables the eddy currents in metal specimens to be demonstrated more directly.

The specimens were made out of brass or copper sheet $\frac{1}{4}$ in. thick and cut into various shapes, and the currents were induced in them by placing them in the field of a vertical a.-c. electromagnet with a laminated iron core. A horizontal insulating platform of glass or ebonite was supported about 2 in. above the top of the electromagnet and the specimens were laid on this so as to be cut more or less normally by the field. A sheet of cardboard, or better still opal glass, sprinkled with very finely divided (for instance, ground) iron was then laid on the top of the specimen.

The use of iron filings in connexion with static fields is, of course, a commonplace, but when used with a.-c. fields they give effects which are much more striking, as the particles forming the pattern are observed to be in continual motion which may take the form of either a violent oscillation or a slow circulation round a closed contour. In the present case the particles are in an alternating field which is partly due to the eddy currents and partly due to the exciting magnet, but it is at once seen that they form themselves into a moving pattern which is closely related to the shape of the specimen used.

Thus figure 1 shows the pattern due to a circular disc 4 in. in diameter and that due to the same disc after it has been slotted with five radial saw-cuts extending half-way in towards the centre. The clear spaces between the arms of this pattern coincide with the radial slots, and the current evidently flows round the slots, while the large peripheral current is very much reduced. The particles in each arm of the

pattern exhibit the slow circulation effect referred to above. This is shown to an altogether greater extent, however, by the use of a specimen in the form of a cross, figure 2. The boundary portion of this figure consists partly of isolated particles

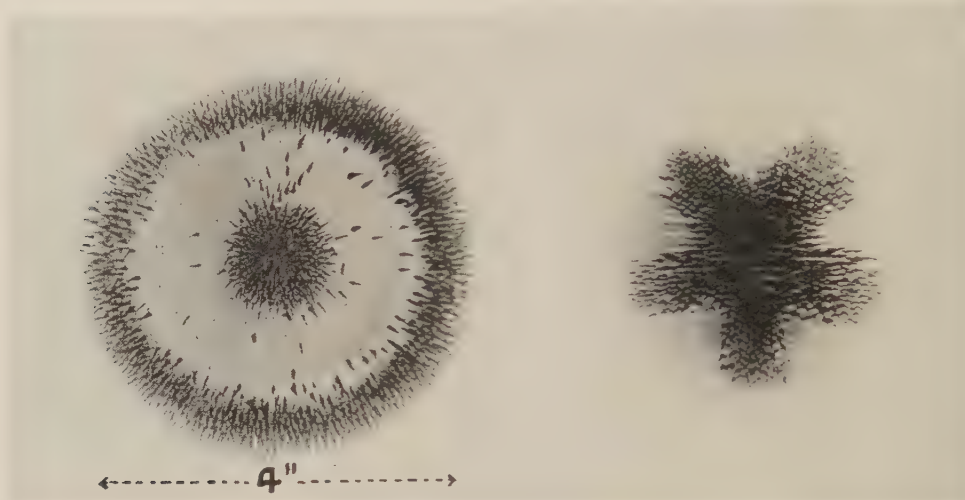


Figure 1.

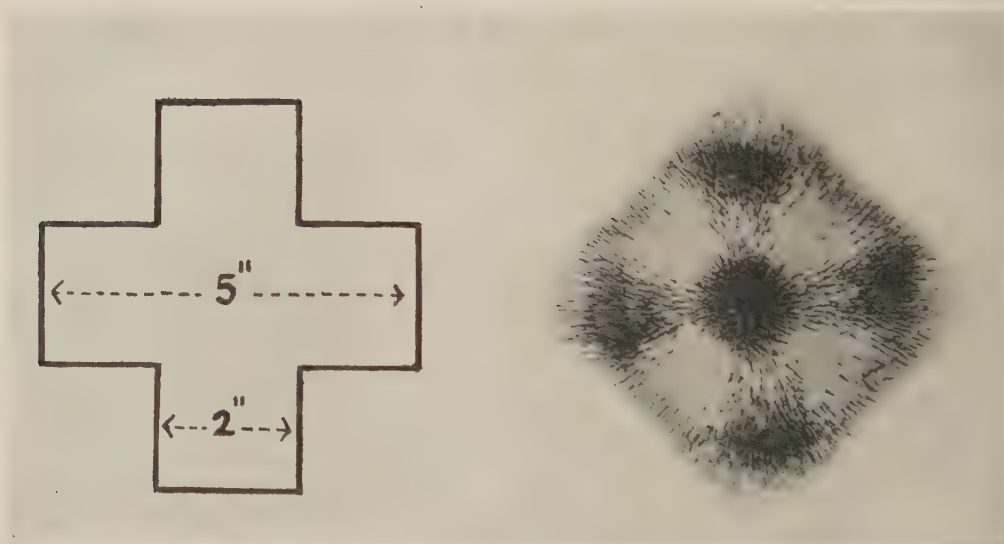


Figure 2.

which are in a state of rapid radial oscillation, and partly of upright needle-shaped aggregates which exhibit no oscillation but gravitate steadily towards the arms of the cross. There they unite to form a continuous stream moving in towards the centre, but as they move the mutual repulsion between adjacent needles keeps them spaced

out like the bristles on a brush. The centre of the pattern is crowded with needles mainly under the control of the exciting field, but the strong mutual repulsion is continually pushing individual members towards the edge of this group, where they become equally affected by both the exciting and the induced fields. These fields are not in phase, so that the needles acquire a violent quivering motion which eventually disintegrates them into a powder which flies out to rejoin the boundary curve. In this way a continual circulation is kept up as long as the field is switched on, and there is no tendency for the material to accumulate at any one point. The resulting pattern represents an equilibrium effect, which may be varied considerably by altering the frequency or the strength of the exciting field.

Although a great variety of results can be produced by experimenting, they can usually be explained by bearing in mind certain governing factors. If we consider the circular disc of figure 1, for obvious reasons the eddy currents will be strongest near the rim of the disc, and the field they produce is the main influence acting upon the outer ring of particles. The central group is controlled by the exciting field, and in between there is a neutral region where neither field can predominate. The power factor for the eddy currents will be nearly unity, and the field they produce will be a minimum when the exciting field is a maximum, and *vice versa*. The powder in the outer ring is thus urged inwards and outwards alternately, and in fact a boundary of this character is found round any specimen in which a large peripheral current is permitted.

There is a certain exchange of particles which goes on between the inner and outer regions, but this exchange assumes much greater proportions in the case shown in figure 2, and it is interesting to see how it is maintained. The relatively clear spaces in this pattern are traversed by an outward streaming of powder produced by the disintegration of the central cluster as previously described, and it is rather surprising that this stream moves uniformly outwards without appearing to be affected by those half-cycles in which the exciting field predominates. The cause of this is probably the increased friction which arises between the particles and the surface during these half-cycles owing to the large downward component of the force exerted on them. When the eddy-current field predominates its action is almost entirely horizontal and the particles are always able to profit by it.

Once the particles have united, however, to form an upright needle they appear to respond much more readily to the exciting field, and one finds (for example in the first pattern of figure 1) a few needles advancing inwards in the face of a stream of powder flowing outwards. A needle seems to be able to behave in this way owing to the fact that its magnetic moment when it is saturated is large in the direction of the exciting field and small in the horizontal direction, so that the eddy field is able to get but little grip on it, and the smallness of the base of the needle makes the frictional resistance less important.

The ability of the smaller particles to ignore the exciting field ceases when they reach the boundary of a figure, and there they oscillate violently backwards and forwards. The divergence of the exciting field may cause it to have an increased horizontal component in these regions, and the frictional factor is lessened owing

to the action being so violent here that the particles are in contact with the surface for only a part of the time.

Whenever a peripheral current in a specimen is large enough to maintain a boundary curve in the pattern, the process of exchange between the inner and outer regions appears to take place. Thus, even with the slotted disc of figure 1, if the slots are made shorter (for instance, one third of the radius) the pattern acquires a circular boundary and a circulation like that described for figure 2 ensues.

The a.-c. magnet employed had an iron core 2 in. in diameter and took about 80 watts at 230 volts; the frequency of the alternating current was varied from 40 to 60 \sim . An ordinary electromagnet with a solid core could probably be used for short periods. Ordinary iron filings do not seem to be suitable for the experiments; a finer type of particle is required. As specimens for showing circular eddy currents a set of rough brass weights served excellently, and doubtless many other variations will occur to any experimenter.

DISCUSSION

Dr L. F. BATES said that modern magnetic alloys gave better results in experiments of this kind than the traditional iron filings. After reading the paper he had tried the experiment with mu-metal dust and obtained good results; but he had obtained a still more striking improvement by mixing mu-metal dust with iron filings.

535.338:546.57

THE ABSENCE OF FINE STRUCTURE IN THE ARC SPECTRUM OF SILVER

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Communicated by Prof. A. Fowler, F.R.S., April 5, 1933.

Read in title May 19, 1933

ABSTRACT. The arc spectrum of silver, produced in a water-cooled hollow-cathode discharge, has been examined for fine structure with a variable-gap silvered Fabry-Perot interferometer in the region 8300 to 4000 Å. Results for the resonance lines at approximately 3300 Å. are also quoted. Silver consists of two odd isotopes 107, 109, and although $5s$, $6s$, $7s$, $5p$, $6p$, and $5d$ terms have been studied no trace of fine structure has been found, in spite of very excessive over-exposing in many lines. All lines are extremely sharp and are worth considering as wave-length standards, being well distributed. Attention is drawn to the fact that the analogous spectrum of Cd II also shows no fine structure, so that it is concluded that the absence of structure is probably due to the electron configuration and not necessarily to smallness of the nuclear magnetic moment. This is remarkable, for penetrating s electrons are involved in some configurations.

§ 1. INTRODUCTION

A NUMBER of previous investigators have examined the important lines of the arc spectrum of silver* for fine structure. In no case, however, have both the source and the interferometers been such as to give very high resolution, so that a thorough re-examination of the spectrum has seemed desirable. The atomic weight of silver is 107.88, and as Aston† has shown that there are two odd isotopes 107, 109 the calculated abundance ratio is 1 : 1 if the mass defect is taken approximately as about 0.13, which, from the position of silver on the mass curve, is what it will roughly be. As both the isotopes have odd atomic weights it is natural to assume that they possess nuclear spins. Many terms of the silver arc spectrum involve deeply penetrating electrons, so that according to expectations the spectrum should show fine structure due to nuclear spin. No evidence of fine structure, however, has been found. The mass isotopic shift will be far too small to be observable and need not come into consideration.

§ 2. EXPERIMENTAL RESULTS

The spectrum was excited in a hollow cathode of silver, some 40 mm. long and with an 8 mm. bore. Helium was continually circulated through the tube at an approximate pressure of 1 mm. and as the gas passed through a charcoal trap immersed in liquid air, a high degree of purity was maintained. The tube was

* S. Frisch, *Z. f. Phys.* **71**, 59 (1931), etc.

† *Proc. R. S. A.*, **115**, 487 (1927).

excited by means of a small generator supplying 1000 volts d.c., and currents of either 200 or 300 mA. were used. The cathode was cooled with a continuous water flow. With this arrangement the tube radiated only the helium lines and the silver arc spectrum, the lines of the latter being very intense and very sharp indeed.

Since most of the important silver arc lines (excluding the resonance lines) lie in the infra-red and visible portions of the spectrum, a silvered Fabry-Perot interferometer was used to examine the lines for fine structure. The interferometer was the Hilger N 71 and was crossed with a large glass two-prism spectrograph of big aperture, the dispersion of which was about 30 Å. per mm. at 5000 Å.* The largeness of the apertures of both spectrograph and interferometer resulted in a very fast combination.

The interferometer was silvered by the evaporation process described by R. Ritschl†, the acid after-treatment being carried out in detail. In the blue and violet regions Ilford Monarch plates, in the green and red Ilford Hypersensitive Panchromatic plates, and in the infra-red Ilford Infra-red Sensitive plates were used‡. Exposure times varied considerably, the green lines being so intense that one to two minutes sufficed for normal exposure, but the infra-red lines required an hour. Photographs extending up to four hours were taken for all regions so that faint components should not be missed.

The line transitions which have been observed are shown in figure 1. The two ultra-violet resonance lines could not be studied, but the author has had the privilege of examining photographs of these lines taken with 25- and 35-plate reflection échelons by Mr W. E. Williams of King's College, London.

The term scheme in figure 1 shows that the following terms come into consideration.

$5s\ ^2S_{\frac{1}{2}}$	$6s\ ^2S_{\frac{1}{2}}$	$7s\ ^2S_{\frac{1}{2}}$
$5p\ ^2P_{\frac{1}{2}}$		
$5p\ ^2P_{\frac{3}{2}}$		
$5d\ ^2D_{\frac{3}{2}}$	$6d\ ^2D_{\frac{3}{2}}$	
$5d\ ^2D_{\frac{5}{2}}$	$6d\ ^2D_{\frac{5}{2}}$	

One of the terms is involved seven times, one five times; five are involved twice and the remaining two once, so that there is ample opportunity for checking conclusions as to term structures.

All the lines which have been examined are given in the table, the allocations being those given by Blair§. Five of the observed lines have not yet been allocated.

* The spectrograph was that bequeathed to the Royal College of Science by the late Col. Gifford.

† *Z. f. Phys.* **69**, 578 (1931).

‡ The author is indebted to Dr Bloch of Messrs Ilford Ltd., for supplying him with a new type of plate not yet marketed. This plate is very fast and as it needs no ammonia sensitization is entirely free from fog.

§ *Phys. Rev.* **36**, 1531 (1930).

|| H. Kayser, *Handbuch der Spektroskopie*, Bd. 7, gives a close neighbour to 4620.0 Å.

Table

Wave-length	Classification	Wave-length	Classification
8273.7	$5p\ ^2P_{3/2}-6s\ ^2S_{1/2}$	4476.1	$5p\ ^2P_{1/2}-7s\ ^2S_{1/2}$
7668.1	$5p\ ^2P_{1/2}-6s\ ^2S_{1/2}$	4311.1	
5471.5	$5p\ ^2P_{3/2}-5d\ ^2D_{3/2}$	4212.7	$5p\ ^2P_{3/2}-5d\ ^2D_{3/2}$
5465.5	$5p\ ^2P_{3/2}-5d\ ^2D_{3/2}$	4210.9	$5p\ ^2P_{3/2}-5d\ ^2D_{3/2}$
5209.1	$5p\ ^2P_{1/2}-5d\ ^2D_{3/2}$	4085.9	
4874.1		4055.3	$5p\ ^2P_{1/2}-5d\ ^2D_{3/2}$
4848.1			
4668.5	$5p\ ^2P_{3/2}-7s\ ^2S_{1/2}$	3382.9	$5s\ ^2S_{1/2}-5p\ ^2P_{1/2}$
4620.0		3280.7	$5s\ ^2S_{1/2}-5p\ ^2P_{3/2}$

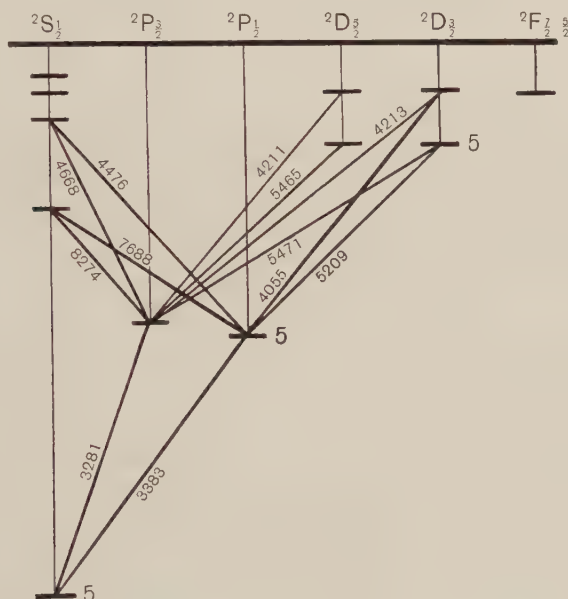


Figure 1. Transitions observed in the arc spectrum of silver.

The instrumental resolution between 4400 and 4000 Å. is not, of course, so good as that for the longer wave-lengths, but it is still quite good enough to show effectively whether appreciable structures exist. The lines were examined with interferometer gaps up to 25 mm. but in no case was any trace of structure found. Indeed, the lines were so sharp that it was not considered that an increase in the interferometer plate-separation would serve any purpose whatever. A number of the lines were also very heavily over-exposed, but no faint components were seen. It is quite certain that all the lines observed are single, and furthermore are so extremely sharp, bright, and well distributed that they could be used as wave-length standards with considerable advantage*.

* The line $5p\ ^2P_{1/2}-6s\ ^2S_{1/2}$ is somewhat broad, and a very narrow doubling is suspected. This would be due to $6s\ ^2S_{1/2}$.

The resonance lines are difficult to produce free from self-absorption effects. The lines photographed by Mr Williams were produced in a water-cooled hollow-cathode discharge, but the cathode was an alloy containing 5 per cent silver and 95 per cent cadmium. The object was to reduce the self-absorption of the silver lines as much as possible without making them unduly weak. The lines are definitely broadened but show no other sign of structure, and it is very probable that the broadening is due to partial self-absorption. If any structure exists it is certainly considerably less than 0.050 cm^{-1} .

It is therefore concluded that none of the observed lines of the silver arc spectrum shows any appreciable fine structure at all.

§3. DISCUSSION OF RESULTS

Before discussing the peculiar absence of fine structure we may first call attention to the work of Wali Mohammad and Sharma* on the silver resonance lines. These authors claim to have found that both lines have almost exactly the same fine structure, namely two strong components 0.218 cm^{-1} apart and a faint component about five times less intense further towards the violet. It follows from this that the structure of the resonance lines is the same as the structure of the $5s \ ^2S_{\frac{1}{2}}$ term. On theoretical grounds this is quite impossible, for the maximum possible number of components is two, since the term multiplicity is $2J + 1$ and $J = \frac{1}{2}$. Even with the assumption that an isotope displacement effect produces the structures four components should result, and the intensities would be quite different, the maximum possible intensity-ratio of any pair of components never exceeding $3.0 : 1$. In the event of the nuclear magnetic moments being such that the weaker components fall together there should be three lines with intensities in the ratio $3 : 3 : 2$, so that every possibility is theoretically excluded.

When the observations of Mr Williams are taken into account it is quite obvious that the reported structure is nothing more than a case of self-reversal. The fact that two equally intense components result (together with the faint line) is evidence of this. None of the components appears in the water-cooled hollow cathode. The source used by Wali Mohammad and Sharma (a vacuum arc) is much more liable to produce reversal.

As regards the present observations, it will be seen that these are very difficult to explain. It is quite certain that silver consists of two odd isotopes and both should possess nuclear spins; for every odd atom so far investigated has been shown to have a nuclear mechanical moment, although the nuclear magnetic moment may be small. The terms examined are produced by the $5s$, $6s$, $7s$, $5p$, $6p$, and $5d$ electrons. The first three of these are penetrating electrons and the fourth may be considered as partly so, because the separation between the $^2P_{\frac{1}{2}}$ and $^2P_{\frac{3}{2}}$ terms is 203 cm^{-1} . This large gross-structure multiplet separation would suggest that the coupling between l and j should be large. It follows from this that, if the silver nucleus possesses an average nuclear magnetic moment, i.e. if the $g(I)$

* *Ind. J. Phys.* 6, 75 (1931).

factor is not abnormal, measurable fine structures are to be expected, particularly in the *s*-electron terms.

The absence of structure can only be attributed to one of two causes; either (1) the nuclear magnetic moment is small, or (2) the coupling between the nucleus and all the external electrons, even penetrating *s* electrons, is small. With reference to these two points, attention is drawn to some unpublished results of Mr E. G. Jones on the spectrum of Cd II. This spectrum is analogous to that of Ag I, the two spectra being in fact, in iso-electronic sequence, and Jones has observed terms practically identical with those reported here for Ag I. In no line has any fine structure been found. As the Cd I spectrum shows very wide fine structures in suitable terms, the cadmium nucleus must possess a large nuclear magnetic moment, Jones concludes therefore that the absence of structure in Cd II must be entirely due to the electronic configuration, or else to some nuclear change in the process of ionization. The latter is highly improbable, judging from work on bismuth and like elements. If the electron configuration of Cd II is such as not to produce fine structures, the same should hold true for Ag I. This fact is very surprising indeed, for, as has been pointed out, penetrating *s* electrons are involved in many terms, and in others the gross structure multiplets are wide.

Any conclusions made about the $g(I)$ factors of nuclei must be carefully considered in the light of the present observations. It appears that the presence of penetrating electrons or large gross-structure multiplets is not evidence enough for assuming that the coupling between *J* and *I* will be large. It has always been previously assumed that penetrating *s* electrons will give easily measurable structures, but the present facts contradict this assumption. It may be observed, too, that the extreme sharpness of the Ag I lines shows that no isotopic displacement effect exists.

§4. ACKNOWLEDGMENTS

The author wishes to express his thanks to Mr W. E. Williams and Mr E. G. Jones for permitting the use of unpublished data. His thanks are due to Prof. A. Fowler, F.R.S., for encouragement and help.

DISCUSSION

Prof. A. O. RANKINE said that confusion was likely to arise between the symbols for silver iodide and the neutral silver atom, both being denoted by AgI. Would it not be better to write Ag.I for the atom?

Dr W. JEVONS. The observations of the lines $\lambda\lambda 3281$ and 3383 to which the author refers are described in a letter by W. E. Williams and A. Middleton in the current number of *Nature*, which also contains a letter by D. A. Jackson recording similar observations of these two lines and five others of neutral silver*. Both investigations agree with the author's in denying the existence of fine structure such as

* *Nature*, **131**, 691-2 (1933).

has been reported by other observers using an unsuitable source. I would like to endorse the President's remarks about the unsatisfactory nature of the symbols which are very widely used to denote emitters of line spectra. Many besides chemists have been misled by the representation (especially in the titles of papers) of a neutral atom M by the notation MI which should surely be reserved for the diatomic iodide. It is true that in many publications care is taken to separate the roman numeral from the chemical symbol by a narrow space, but even this is sometimes not insisted upon. It would be far better to write the numeral in smaller type, either on the same line as the chemical symbol (MI, MII, ...), or as a superscript (M^I , M^{II} , ...), or as a subscript (M_I , M_{II} , ...); the first of these alternatives has, indeed, been adopted by many authors, e.g. in the *Astrophysical Journal*. Since it has become known that the successive stages of "simplification" of the atom, which Sir Norman Lockyer first represented by MI, MII, MIII, MIV, ..., are the neutral, singly ionized, doubly ionized, trebly ionized, ... atom (resulting from the loss of none, one, two, three, ... negative electrons), it is a great pity that these symbols are not abandoned in favour of M, M^- , M^{--} , M^{---} , ..., where the unadorned M represents the neutral atom. This plan has been adopted in the literature of molecular spectra; although the molecules concerned are only neutral and singly ionized, the introduction of such symbols as HClI and HClII for what we denote by HCl and HCl^+ would have been unfortunate, to say the least. For some atomic emitters the replacement of the usual notation by one of the alternatives mentioned here is particularly desirable; consider, for example, the atoms and atom-ions of iodine and vanadium.

AUTHOR'S reply. In reply to Prof. Rankine: It is not customary to write a dot between the Ag and the I when referring to the neutral silver spectrum. Instead a space is left, the symbol being written as Ag I. The fact remains that this may still be confused with the symbol for silver iodide, but unfortunately it is the regular practice of most spectroscopists.

In reply to Dr Jevons: The alternative suggestion of writing + signs instead of Roman numerals to designate multiply ionized spectra is used by some authors. The main objection is that the symbol becomes cumbersome with high degrees of ionization, and indeed a visual mistake is easy. Compare for instance the two notations in the case of bromine which has had six electrons removed by excitation, e.g. Br VII and Br+++++,.

Dr A. FERGUSON suggested the use of the following more compact notation: Ag, Ag^+ , Ag^{2+} , Ag^{3+} , ... Ag^{n+} .

THE MEASUREMENT OF VISUAL SENSATIONS

BY N. R. CAMPBELL, Sc.D., F.INST.P.

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ABSTRACT. The paper is a criticism of Dr L. F. Richardson's proposed method of measuring sensations by "mental estimates". In the absence of agreed principles the discussion is conducted in the light of an analogy with thermometry.

It is argued (1) that Dr Richardson's own facts prove that the method of mental estimates is inferior to another available method of measuring the same thing. If his facts and his implied propositions are true, indirect measurement by means of his *S* must be preferable to direct measurement by *R*. (2) That any arguments that Dr Richardson might base upon the fact that his method of measurement leads to a numerical law between *R* and *S* would be valid only if he proved that this law is true and not empirical. (3) That if his method measures anything, that something is almost certainly not a sensation; at least, that he has provided no evidence that it is a sensation.

Finally it is pointed out that Dr Richardson's method indicates the theoretical possibility of a method of measurement based upon ordering differences of increasing degree; but there is no evidence that the method is ever practically possible.

§ 1. THE PROBLEM

IN the discussion on Vision organized by the Physical and Optical Societies on June 3, 1932, of which a report has been issued, the question was often raised whether visual sensations are measurable. But it was never discussed in the light of any general theory of measurement; indeed the only speaker (namely Dr L. F. Richardson, pp. 112-116 of the report) who referred to any such theory (namely my own) deliberately rejected it. The natural conclusion is that physicists generally hold that no general theory of measurement is possible or, at least, that none has yet been established. Of course I do not agree with that conclusion; I think that theories already propounded give a very simple and direct answer to many of the problems that were raised; and that where they fail to provide an answer, the failure lies, not in the theories, but in the ambiguity of the term "sensation." However it would be absurd to consider doctrines in the light of principles that are almost universally rejected; and some other basis must be found for the criticism that I want to offer. Such a basis may perhaps be found in analogy; if we can show that some proposed method of measuring sensations violates conditions that confer its validity on some accepted system of measurement, then we shall clearly throw doubt on the validity of that method.

The only proposed method of measurement that I am going to consider is that of Dr Richardson, though I believe that the arguments advanced have a bearing on the views propounded by other speakers. This method is called by its author that of

"mental estimates"; I venture to prefer the simpler term "measurement by guessing." The accepted method of measurement that I shall choose as a guiding analogy is thermometry.

§ 2. THE ANALOGY

If a number of persons dip their fingers into a set of basins of water at different temperatures, each will be able to arrange them, confidently on the whole, but with some doubt in particular cases, in a definite order of warmth; and there will be a strong resemblance between the orders adopted by different observers. Indeed it is probable that it will never happen that one observer declares confidently that *A* is warmer than *B*, while another declares with equal confidence that *B* is warmer than *A*. Further the observers can probably be induced to represent the basins by points on a straight line, the ends of which represent the hottest and the coldest basin, in the manner described by Dr Richardson. The order of these points will, of course, agree to the same extent; and the range covered by the points assigned by different observers to represent the same basin will be much less than the whole length of the line, and not very much greater than that covered by the points assigned to the same basin by the same observer at a number of successive trials separated by an interval so long that memory plays no part.

§ 3. WHY IS THE ANALOGY NOT MEASUREMENT?

But such measurement by guessing is not the standard method of measuring temperature; we do not take *R*, the mean distance of a representative point from one end of the line, as the measure of the temperature of a basin. Why? Dr Richardson would reply, I think: Because we have a better way of measuring temperature; if we had no better way, *R* would measure temperature. Now that answer implies two propositions: (1) that there can be two ways of measuring the same thing; (2) that the purpose of measurement is something in which accepted methods of measurement excel guessing. Further I think he would admit that this something is primarily sensitivity (though he might prefer to call it accuracy). If we compare (say) platinum-resistance thermometry with guessing, the striking difference is that by the former we can distinguish basins that are indistinguishable by the latter; the thermometer can say definitely that one basin is warmer than another, when direct sensation detects no difference at all.

§ 4. MEASUREMENT AS NAMING

If that is so, we can reach our first conclusion. It is that one purpose at least of measurement is to distinguish things. The numerals assigned in measurement are, in part at least, names. In this respect a method of measurement would be ideal if it always led us to assign exactly the same numeral, the same name, to the same object, and always to assign different numerals to objects that are in any way distinguishable in the property we are considering. The second part of this ideal is

attainable. For every measurable property there is one most sensitive method of measurement (or possibly a group of such methods all equally sensitive and more sensitive than any other). If we adopt that method, then we shall never assign the same name to distinguishable things; and we have no right to adopt any other method, except for professedly provisional purposes, or to regard it as really constituting measurement. On the other hand, the first part of the ideal is usually unattainable. In all but a small group of measurements, the most sensitive method will sometimes lead us to assign different numerals to the same thing; that is due to what is called experimental error. Accordingly we need not demand that a proposed method of measurement fulfils the first part of the ideal.

§ 5. WHEN ARE TWO MAGNITUDES THE SAME?

We must now return to the proposition called (1) above. What is the criterion by which we are to determine whether two methods of measurement measure the same thing? This question has often been asked; many people seem to find a strange difficulty in answering it. To me the answer seems perfectly clear, and to depend on the conception of order; this conception must be fundamental in measurement, because the obvious reason for giving to numerals a unique position as names is their possession of a very definite and complete kind of order. My answer is that two methods measure the same thing, if the order of the numerals assigned by one to the members of a group is always the same as the order of the numerals assigned by the other to those same members. If, and only if, that is so, there is a definite and significant one-one relationship between the names assigned by the two methods. But one proviso must be added. The orders assigned by two methods differing in sensitivity can never be exactly the same; for one will distinguish things that the other confuses. Unless we are to confine the term measurement entirely to the most perfect methods, and refuse to recognize imperfect methods as measurement at all, we must add that differences of order arising inevitably from the ambiguity of the less perfect methods are negligible. Methods are the same if, and only if, their orders are the same as far as the ambiguity inherent in any of them permits.

According to this criterion platinum thermometry and guessing measure the same thing (subject to certain reservations raised in § 8, which enforce our ultimate conclusions). But let us carry our analogy with Dr Richardson's work a step farther, and suppose that the basins are prepared by mixing in them S parts of hot water with $100 - S$ parts of cold water, S being measured. The order of R , the numeral assigned by guessing, will be found to agree, apart from ambiguity, with the order of S . If R is plotted against S a smooth curve will be obtained. But do S and R measure the same thing, according to the criterion? If basins are never prepared otherwise than by mixing the hot and cold water, the answer is, Yes. But we must note two possibilities. (a) We might prepare by other means basins of water precisely similar to those produced by mixing, e.g. by heating cold water with a flame. (b) We might prepare objects of other kinds, e.g. basins of oil or even solid bodies, that could not be simulated completely by mixing hot and cold water, and yet could

be "measured" in exactly the same way and included in the same order with the basins of water. If we take these possibilities into account, the order of *R* is not always the order of *S*; for there may be no *S*. Accordingly, especially in view of possibility (*b*), we should say that *S* and *R* do not measure the same quantity. But we must note also (*c*) that we could always prepare by mixing hot and cold water, a basin, characterized by a definite *S*, which would be equal in temperature to, and have the same value of *R* as, any of the objects that had not been, or could not be, prepared by that process.

In these circumstances, I think our attitude would be this. *S* and *R* are not the same thing. But by measuring the *S* of a body having the same temperature as a body which can otherwise be measured only by *R* (for the moment we are ignoring platinum and other thermometers), we obtain a more sensitive way of measuring the thing measured by *R*. For *S* is actually less ambiguous than *R*; and the ambiguity in deciding whether two temperatures are equal is less than that in assigning *R*'s to them. Though *R* may be a way, even the only way, of measuring the thing directly, *S* measures it indirectly; and the indirect method is the better; it is to be preferred always, except when we are temporarily content to put up with imperfection.

§ 6. FIRST CONCLUSION

The analogy is incomplete only because, in Dr Richardson's work, possibility (*b*) is absent and perhaps possibility (*a*). (I simply do not know whether a series of differently saturated hues can be prepared otherwise than by mixing a saturated hue with white.) The absence of these possibilities makes it less plausible to maintain that *R* and *S* are not the same thing; but, whether they are or are not the same thing, possibility (*c*) makes it quite certain that measurement by *S*, even if it is indirect, is a better way of measuring what *R* measures than direct measurement by *R*. Our conclusion then is this. Dr Richardson's advocacy of his proposed method of measuring sensations rests on the smooth curve that he obtains between *R* and *S*. But that proves only that *S* and *R* have the same order, apart from ambiguity inherent in *R*. But that, in its turn, gives rise to a strong suspicion that *R* measures the same thing as *S*, so that his proposed method measures a "stimulus," not a sensation; and it proves quite definitely that, even if *R* and *S* are not the same thing, the best way to measure what *R* measures, is *not* by his method, but by the indirect method involving *S*. In other words his facts prove the exact opposite to his conclusion.

§ 7. MEASUREMENT AND NUMERICAL LAWS

So far we have assumed that the purpose of measurement is distinction and identification. And that is certainly one purpose. But if we return to our analogy we shall see that there is another. (If a psychologist reads what follows, he may not understand the references to "fixed points" and "thermodynamic scale"; but he need not understand more than the conclusions drawn.) Platinum-resistance

thermometry requires four fixed points. Numerals can be assigned to other temperatures with the same sensitivity and definiteness, whatever numerals are assigned to these points. Actually however we do not regard it as providing satisfactory measurement, unless they are so assigned that the scale agrees with the thermodynamic scale. Why?

The reason is that one of the purposes of measurement is to enable us to discover numerical laws between things measured. Physicists do not regard a law as a true numerical law, unless its form is simple and/or explicable by a theory; if it does not fulfil that condition, it is a mere empirical law. It is a fact that we do not arrive at true, as distinct from empirical, laws involving temperature, unless we choose the fixed points so that the numerals assigned by platinum thermometry agree with the thermodynamic scale.

It appears to me that part of Dr Richardson's arguments in favour of his measurement by guessing (he never states them definitely) are based on this purpose of measurement, the formulation of numerical laws. He argues that his relation between S and R is a numerical law, and that therefore the process of assigning numerals on which it rests, since it fulfils this purpose of measurement, must be measurement. If he produced any evidence that his law is a true, and not an empirical, law, the argument might have some weight, though it would never be conclusive. But in the absence of that evidence, it is of no value at all. Any process of assigning numerals in respect of a property capable of order, in accordance with that order, can hardly fail to lead to an empirical numerical law relating the property to some other. But the process of assigning numerals in accordance with an order is not necessarily measurement; if it were, the "numbering" of houses in a street would be measurement. If Dr Richardson is going to introduce at all the conception of a numerical law—a distinctively physical conception—he must accept the general standpoint of that science. In physics it is quite certain that a process of assigning numerals is not regarded as measurement, unless it fulfils conditions more stringent than the mere representation of order. The fact that a process leads to a true numerical law may possibly be evidence that these more stringent conditions are fulfilled; the fact that it leads to an empirical law most certainly is not.

§ 8. IS R A SENSATION?

So far we have been inquiring whether R measures anything. If we had answered that question affirmatively, it would still have been necessary to inquire whether it measures a sensation. A few remarks on this matter may still be made; fortunately some of them are independent of any knowledge of psychology.

If the line along which Dr Richardson's observers are asked to place their points is necessary to the "measurement" of R , then what R measures is certainly not a sensation; for nobody will pretend that a straight line is a constituent of a sensation of hue. The line would be necessary, if it turned out either that observers refused to assign numerals directly instead of indirectly by means of the line, or that the numerals assigned directly differed systematically from those assigned indirectly.

It seems almost certain that the value of R assigned to a hue depends on the group of hues with which it is associated as well as on the hue itself. If the same hue X were presented, first, with a group all less saturated than X and, second, with a group all more saturated than X , surely the R assigned to X would tend systematically to be greater in the first case than in the second. If so, R (if it is concerned with sensations at all) measures some compound of a particular sensation and of a group of sensations.

Again, it is probable that R depends on the order of presentation, either in time or space. If a group of hues, containing a pair X and Y , so similar as to be just distinguishable, were presented in random sequence, it would sometimes happen that the values of R assigned were in the wrong order. But if X and Y were always presented in immediate juxtaposition, such a mistake would be made much less often. If so, R measures a compound of a sensation and of the order of presentation of a group of sensations.

Lastly, it is remarkable that Dr Richardson combines the values assigned by many different observers who differ systematically. Here psychological questions are involved. But if, as seems at least plausible, a sensation is something characteristic of a single individual, this procedure is not justifiable, unless some criterion is laid down to determine when the sensations of two individuals are the same or are equal. One conceivable criterion is that individuals exposed to the same stimulus experience the same sensation; this criterion might justify Dr Richardson's practice of taking the mean of the R 's assigned by different observers; but it is inconsistent with his deliberate statement that observers differ in their sensations of the same stimulus. Another conceivable criterion is that observers experience the same sensation when they react in the same way. But then the systematic difference between observers shows that there can be no law between R and S ; for R is the reaction, and different S 's are undoubtedly associated with the same R . I can discover no criterion that is not either utterly unreasonable or inconsistent with Dr Richardson's practice.

§ 9. FINAL CONCLUSION

To sum up, there is no reason to believe that R , if it measures anything, measures a sensation, and much reason to believe that it does not. Again, if it measures something, that something is not certainly different from the stimulus S , and is certainly something that is measured more satisfactorily by an indirect process, involving S , and not by the direct process of guessing. The only apparent objection to measuring this something by means of S is that it then becomes impossible to state a numerical law between S and R . But, since there is no evidence that the law that Dr Richardson proposes is true and not merely empirical, this objection has no weight.

In fact, I think the position can be summed up by another analogy, which I hope will not be thought too frivolous. I know a street in which the houses are numbered and graduate definitely from fine houses with large gardens at one end to something like slums at the other. I believe that the citizens of the town in which it lies could

be induced (even in these days) to represent the social position of the occupants of those houses by points on a line, and thus to assign values of R to them, according to Dr Richardson's plan. If so, the R values of the occupants plotted against the numbers of the houses would give a definite curve. But, in my submission, that does not prove that the numbering of houses is measurement or that the problem of measuring social position independently of wealth has been solved. The most that it proves is that the conventional estimate of social position is influenced largely by the character of the house occupied.

§ 10. MEASUREMENT BY ORDERING DIFFERENCES

One last word. I may seem to have proved too much. Surely, an objector may say, there is some significance in the fact that observers agree so well in their "mental estimates." Certainly; it may be a very interesting psychological fact; but Dr Richardson has not produced any evidence that it is significant in the problem of measuring sensations. Again, he may say, surely there must be some meaning in the fact that the curve relating S and R is not a straight line, but has definitely some other form. This objection requires rather more attention.

The curvature of the (S , R) line arises from our power of ordering, not only hues, but also differences between hues. Almost everyone will agree, not only that a buttercup is yellower than milk and milk than snow, but also that the difference between a buttercup and milk is greater than the difference between milk and snow. Now it can easily be shown that if we could order in this way all the differences between sensations, that is to say not only first differences, but also second differences, third differences, and so on indefinitely, then a process of measurement would be possible by means of which we could assign numerals quite uniquely. (Perhaps I had better explain, for the benefit of the possible psychologist reader, that second differences are differences of first differences and so on.) A simple example will show what I mean. If we have 5 hues, A , B , C , D , E , and a choice of the numerals 0 to 10 to assign to them, and if we know that the hues stand in that order, then we can assign the numerals in many ways, so that the order of the numerals agrees with the order of the hues. But if we know also that the differences between the hues stand in the order $A-B$, $B-C$, $C-D$, $D-E$, then we have only one choice; the assignment must be A 10, B 6, C 3, D 1, E 0. If we knew the order of the second differences, the choice would be uniquely determined, even if we had more numerals at our disposal. Here is a system of measurement theoretically possible; the algebra of it is simple, but need not be elaborated. For as a matter of fact, we can rarely, if ever, order any differences higher than the first or second. Dr Richardson's curve is merely an indication that, in this case as in many others, we can order first differences; it provides no evidence that we can order any of the higher differences that must be ordered if measurement by guessing is not to be inferior to substitutes already available.

DISCUSSION

Dr R. T. BEATTY. As a physicist I agree with Dr Campbell's view that physical measurements are most accurately performed by methods of coincidences or of equality of sensations. But such methods cannot be employed to compare, numerically, sensations of different magnitude: such comparisons are apparently intuitive; their accuracy can neither be confirmed nor disproved by any other individual, and as a rule the individual who makes them is unable to indicate the factors on which he bases his numerical comparison.

Many people are able to compare the loudness of sounds. Experiments carried out by Ham and Parkinson* with 175 observers showed that with two pure tones of the same frequency an intensity ratio of 8 to 1 corresponded to a loudness ratio of 2 to 1, and this relation held good over a large range of intensity. Similar results were obtained by Richardson and Ross† though the scatter in their experiments was considerable. In the domain of vision I have made experiments on 50 observers. With the eyes in a definite state of light-adaptation, two lights of the same colour were flashed in rapid succession on a screen, the duration of each flash being one second, and comparisons were made of subjective brightness. When the illumination ratio was 8 to 1 the subjective brightness-ratio was on the average adjudged to be 2 to 1.

This agreement may appear to be merely a coincidence. But in view of what physiologists tell us about the similarity of response of sensory nerves, whether excited directly or by means of a stimulus applied to their end-organs, we may suspect a relationship.

A most interesting result has been obtained by Adrian‡, who measured the number of nerve impulses produced per second when the optic nerve of a vertebrate was stimulated by light falling on the retina. Under steady illumination adaptation occurred and the frequency of the impulses decreased, but if we consider only the initial outburst of impulses we find from Adrian's curves that when the intensity-ratio of illumination is 8 to 1 the corresponding numbers per second of nerve impulses are in the ratio of 2 to 1.

From these results one may be justified in stating the following hypothesis. When two sensations of loudness or of subjective brightness are mentally compared as a numerical ratio, the ratio is based on, and its value is comparable with, the ratio of the frequencies of the nerve impulses which evoke the sensation.

How is the numerical ratio transferred from nerve to mind? I suggest that it is by experience of muscular sensations. The relation between weight lifted and number per second of afferent nerve impulses from the muscles concerned is one of simple proportion, unlike the relation found by Adrian in the case of vision. A muscle is composed of individual fibres, each of which is either relaxed or completely contracted. If 10 fibres must contract when a 1-lb. weight is lifted, 20 are re-

* *J. Acoust. Soc. Amer.* 4, 511 (1932).

† *J. Gen. Psychol.* 3, 288 (1930).

‡ *J. Physiol.* 63, 378 (1927).

quired for 2 lb., with a corresponding doubling of the number of nerve impulses per second. The sensations evoked are correlated with the knowledge that in one case one object is lifted, while in the other case two similar objects are lifted, and so a numerical ratio is assigned to the magnitudes of the sensations, a ratio which is identical with the ratio of the frequencies of the nerve impulses.

If we assume that this interpretation of sensory messages is transferred more or less accurately to the domains of hearing and vision, we have an explanation of the experimental results already mentioned.

Mr R. J. BARTLETT. From one point of view measurement is a scale reading—the distance from a datum. In measurement a scale is presupposed. Now a scale of orangeness might be prepared by continued division of the distance between yellow and red by the method of equal-appearing intervals. A scale of the same number of points could be prepared by the quantitative mixing of red and yellow as on the colour wheel. If the various points on the one scale are approximately identical with those on the other, it would be reasonable to accept the physically determined scale rather than the psychologically determined scale as the more accurate. If, however, there is a marked difference between the two, the psychologically determined scale must be accepted as the more correct scale of orangeness, and interest will centre in discovering, if possible, a law that will connect the two scales and so enable the more consistent physically-determined scale to be converted into a scale that is psychologically true.

Mr J. GUILD. Dr Campbell's paper deals with a subject which, at first sight, does not appear to offer much interest to physicists as a whole. Direct interest in these problems among physicists is probably confined to those who work in branches of optics and acoustics in which there is some overlap between physics, physiology and psychology. Nevertheless, discussion of the specific question on which Dr Campbell and Dr Richardson are at variance raises wider issues which ought to be of interest to every member of this Society.

Dr Campbell is the author of the only text-book which has been written on the theory of measurement, so I presume we may take it for granted that every physicist is familiar with his views. Needless to say, on so vast a subject there are minor points on which differences of opinion can arise, and unfortunately one is involved in the present paper. Dr Campbell puts forward the thesis that two methods of experiment measure the same thing if the numerals obtained by them are always in the same order. In my opinion this criterion, while necessary, is not sufficient. Further criteria are necessary, which, though expressible in various ways, originate in the theory of similar relations. I do not, however, wish to discuss this question further and thereby divert attention from the author's main conclusion, which is that whatever the experiments of Dr Richardson and Mr Maxwell actually accomplish they certainly do not "measure sensation."

I am in complete agreement with this conclusion, which necessarily emerges from any method of analysing these experiments, and follows from the fact that there is not a one-one relation between stimulus and sensation.

The entities which enter into these experiments are not identified except by reference to specified stimuli. The observer is presented with three stimuli, S_1 , S_2 and S_3 and finds a certain order to exist among entities which have to be described as "the sensation evoked by S_1 ," "the sensation evoked by S_2 ," and so on. These entities belong to the class of things called *descriptive functions* and cannot be identified with any one of the terms occurring in them. The R s with which the observer experiments are not, therefore, either sensations or stimuli: they are complex functions involving both.

If the relations involved in these functions were known to be one-one (not merely not known to be not one-one) we should be entitled to regard each function as serving to identify a sensation. This would still be insufficient to constitute a method of measuring these functions a method of measuring the corresponding sensations; but we need not discuss this latter point because, as a matter of fact, we know quite well that the relation between stimulus and sensation is not one-one but varies with every alteration in the conditions.

In order to obtain a one-one correspondence it is necessary to extend each descriptive function by inserting an instant of time, obtaining "the sensation evoked by S at the instant t ." The relation "evoked by S at the instant t " is one-one between stimulus and sensation and serves to identify a sensation in the same limited sense that "the word being spoken by Dr Richardson at the instant t " serves to identify a particular word even if we have no knowledge of what word it is.

But it is clear that we cannot interpret the R s which emerge from these experiments as definite descriptive functions of this kind, for immediately we make them definite by specifying instants we also make them ephemeral. Their significance is confined to the specified instants and cannot be maintained throughout a system of relations involving several experiments. Any law emerging from a series of experiments cannot concern the definite functions involving instants, but must subsist between the ambiguous functions which do not involve instants, and which, for that very reason, cannot serve to identify sensations.

The preservation of the identity of the function "the sensation evoked by S_1 ," say, throughout a series of experiments, does not involve preservation of the identity of any sensation. Now it is essential to the meaning of a relation that all the terms which appear in it shall preserve their identity throughout the whole series of operations involved in determining the relation, and, as this is not true of sensation in experiments in which sensations are only indicated by reference to stimuli, any relations obtained cannot be relations subsisting among sensations.

The sensations evoked by the two terminal stimuli to which the observer relates the intermediate member are not, as Mr Maxwell claimed in his remarks, standards of sensation, but are standards of the complex function "the sensation evoked by S "; and the R to which the results apply does not denote the one term, sensation, but denotes the entire function.

It is impossible here to discuss the distinction between a descriptive function and the terms which appear in it, but a consequence of the distinction is that things which are true of the function are not necessarily true, or even significant, when

said of any individual term, and *vice versa*. The function and its terms are entities of different mathematical types, and to confuse "the sensation evoked by *S*" with a definite individual sensation is a gross error in logic.

There is a plentiful field of experiment for psycho-physicists in determining the relations between ambiguous descriptive functions of this type, but a clear appreciation of their meaning is necessary if the interpretation of the results is not to remain permanently obscure.

It will always remain obscure so long as a relation such as that shown by Mr Maxwell's curve is assumed to be a relation in which the related terms are sensations and stimuli. It is a relation in which each value of the independent variable is a stimulus, and the corresponding value of the dependent variable is that member of the class of ambiguous descriptive functions "the sensation evoked by *S*" which is obtained by putting the stimulus in question for *S*. Each sample of the dependent variable itself involves an *undetermined* relation between stimulus and sensation.

All this follows from the nature of the experiment and does not depend on what the observer *thinks* he is doing when he assigns values to the dependent variable. In order to get any further in the process of interpretation, we must consider to what extent the results represent a subjective interpolation of the phenomena *actually existing during the experiments*, and to what extent they are influenced by past experience of the appearances presented by combinations of stimuli.

It would be very difficult for an experienced photometrist or colorimetrist to perform these experiments "honestly." Despite himself his judgment would be influenced by knowledge of the stimulus combinations required to produce appearances similar to those presented to him, and the "values" which he assessed would be little else than estimates of the stimulus ratios. This process is truly, as Campbell suggests, only an attempt to measure stimulus ratios by a rather unsatisfactory method. There are very few members of the community who have not picked up ideas—none the less definite because they are frequently wrong—on the association of appearances with stimulus characteristics. The influence of these ideas on the observer's "answer" cannot be eliminated just by instructing him not to think about them. They would have to be eliminated not only from his conscious intentions but from the records which exist in the neurones of his central nervous system.

In my experience the preconceived ideas of the man-in-the-street on colour-mixing, for example, are not less definite than those of the experienced colorimetrist. They differ from his only in being less nearly in accordance with physical facts. It is possible, therefore, that an inexperienced observer when performing an experiment of this kind is doing exactly the same thing as a colorimetrist would almost certainly be doing; that is, guessing the stimulus ratios, the only difference being that his guesses would have a greater tendency to be systematically wrong owing to the wrongness of his preconceived notions.

I do not see that we can definitely conclude, without further evidence than is contained in the experiments themselves, that the departure from a straight line exhibited by Mr Maxwell's results indicates anything more than a systematic

wrongness in preconceived ideas on additive colour-mixture, based, as are most people's ideas on colour-mixture, on a miscellaneous experience in which subtractive colour-mixing predominates.

I do not suggest that this is all that is involved in the curve, but merely that it is by no means proved that anything else is involved. If it could be shown that similar results were obtained by observers so entirely ignorant of the world they live in as to have no preconceived ideas on anything, we could then definitely conclude that a true subjective ordering of immediately present sensory phenomena was involved; but persons of this kind are hard to find, even among psycho-physicists, and some doubt must, apparently, always remain regarding the extent to which judgment based on memory enters into such experiments.

In conclusion I would refer to a more general matter. Whenever discussions of this kind arise concerning the meanings of words and processes there are always some who regard such discussion as mere "hair-splitting" and quibbling over unessential distinctions. "Let us get on with our experiments," they say; "what does it matter whether we call a process *measurement* or not, or whether we call the things with which we experiment *sensations*, or ambiguous descriptive functions, or anything else; it is the results that matter." This attitude, in my opinion, reaches the limit of absurdity. It is tantamount to the assertion that it doesn't in the least matter that we should know what we are talking about. Results cannot "matter" until we express them in propositions of known meaning. If I assert that I kick a football, this only becomes intelligible because *kick* denotes a certain process and *football* denotes a certain kind of object. If I make an assertion in these words and then qualify it by saying that it doesn't matter whether *kick* means the process which this word usually denotes or *football* the kind of object which this word usually denotes, what fact have I succeeded in describing?

The significance of any asserted fact does not lie in the mere sound or grammatical form of the assertion but in the meanings of the words used and the kind of relations in which these meanings stand to one another.

If we wish to talk about measurement in connexion with sensations, then measurement must *mean* measurement, and sensations must *mean* sensations—the things actually *felt*—and not entities of a different mathematical and logical type. Any statements involving these words but not these meanings can never be anything but sheer nonsense.

Dr W. D. WRIGHT. I hope our ideas on visual sensations will be clarified as a result of this discussion. I was, however, disappointed with the oral remarks of Mr Guild, in whose opinion I have considerable faith. I am afraid I followed very little of his argument, but I did gather that he looked on the measurement of visual sensations as a particular example of some general proposition. This method of attack is usually to the disadvantage of the particular problem. Hence my disappointment. This was the more unexpected as Mr Guild had already dealt clearly with the problem in his discussion of Dr Richardson's original paper. If I may quote, he says there "But we cannot *measure* the magnitude of a sensation. We

cannot experimentally isolate a unit of sensation from which to build up a quantitative scale of magnitude as required by all processes of measurement. This does not mean that we cannot make subjective estimates of the magnitude of a sensation: that in fact is the only means we have of obtaining quantitative information about sensations." With all of this I am in entire agreement. If now we apply this view, it seems to me that the outstanding points of Dr Campbell's paper lose their significance.

For example, Dr Campbell concludes that since R varies with S , in all probability R simply measures S in a bad way. But if R is a mental estimate of the magnitude of a sensation, then it certainly is not a measure, good or bad, of S . It must be one or the other, but it cannot be both, and I think Dr Campbell is wrong in regarding it as a measure of S .

Again, Dr Campbell, quite rightly, assumes that R will vary with the simultaneous or successive contrast to which the eye may be subjected. But to suggest that, assuming R *did* measure a sensation, it would in this case measure a compound of sensations, is quite wrong. R is an estimate of a particular sensation, an entity which, certainly, is affected by the experimental conditions but only as regards its magnitude and not its quality. (We must assume that the colour remains on the same line between white and red.) Hence while the magnitude of the sensation is changed, R is still an estimation of this magnitude and not of any compound of sensations. An analogy may make the point clear. If we had a basket containing a dozen apples, 12 would represent the number of apples in the basket. If, now, a boy came along and stole four apples, there would be eight left. Then 8 represents the number of apples now in the basket, but on Dr Campbell's argument 8 measures a complex function of the apples, the basket and the boy.

I am in partial agreement with Dr Campbell in his argument against combining the values from different observers. Evidently if each individual experienced a marked difference in sensation for the same stimulus, such a combination would be meaningless. For instance, a smooth curve between R and S that was obtained by combining results for a number of normal observers and a number of colour-blind observers would be meaningless. The result would correspond to no known individual. But for observers who have normal vision the mean curve simply represents what an average observer gives as his estimate, and includes the effect introduced by the minor variations evoked by the same stimulus. It is admittedly necessary to assume that these variations are relatively small and distributed about a mean, but Dr Campbell apparently considers that they must be non-existent.

One last point. It appears to me that Dr Campbell's suggested method of measuring sensations by ordering differences is, in effect, the same process as that implied in the Weber-Fechner law, namely the ordering of sensations by observing just-noticeable differences of sensation for varying stimulus. The novelty of the method is therefore doubtful. In any case, as Mr Guild has indicated, we cannot measure sensations, and this method, with any others, must be discarded.

Mr T. SMITH. An essential question involved in this discussion is the meaning, and possibly the need for limitation of the scientific use, of the word "measurement." I should like to express my agreement with the position Dr Campbell has taken up in his book *Measurement and Calculation*, and the view that Dr Richardson's application of the word to mental estimates is unfortunate and inconvenient. The arguments used in this paper must be read in conjunction with the more detailed discussion in Dr Campbell's book, for owing to the need for brevity some conditions essential for the validity of the arguments are not specifically referred to, e.g. the limitation to a closed set of the numbers used to express measurements.

Measurements other than those of derived magnitudes depend upon a procedure by which two magnitudes A and B can be conjoined so as to be equivalent in some respect to a third magnitude C belonging to the same group as A and B . Provided this relation obeys some well-known conditions the process can be assimilated to arithmetical addition, and hence numerical values can be assigned which enable connections to be established with numbers corresponding to other measurable properties. If it were possible to devise a process for synthesizing two sensations so that in some respect they were jointly equivalent to a third sensation we should be able to measure sensations. In the absence of such a process careful examination shows that, whenever real measurement is carried out, it is not a sensation, whatever else it may be, that is being measured.

In investigating estimates of the ratios of sensations Dr Richardson is examining a matter of very general interest, but I suggest that part of his procedure is open to criticism. It may be that some people readily and naturally form definite judgments of the relative intensities of their sensations, but many of us find the process artificial and very uncertain. Sensations sufficiently akin can be placed readily enough in a definite order, an order in which general agreement can be obtained. If, for this discussion, we use the symbols \lessdot and \gtrdot to denote "slightly less than" and "slightly greater than" with respect to some property for which less and greater have been defined, the useful relations between sensations of the same class can to my mind be adequately described by the series of symbols

$$\lessdot\lessdot, \lessdot, \lessdot, =, \gtrdot, \gtrdot, \gtrdot\gtrdot.$$

The only point on which I am uncertain is whether it is not also desirable to add \sim to express the relation between those sensations for which we find it difficult to decide between \lessdot , $=$, \gtrdot owing to the unavoidable intrusion into our consciousness of other properties than the one under consideration. If I may take an example from Dr Richardson's recent paper "A quantitative view of pain"* in place of his scale $A = 3$, $B = 20$, $C' = 30$, $C = 70$, $\alpha = 100$, $D = 200$, $E = 500$, $\beta = 500$ (C' represents C when the sufferer's attention was distracted from his pain), I should probably not be able to say more than

$$A < B \lessdot C' \lessdot C \lessdot \alpha < D < E = \beta.$$

We hear children make such remarks as that one kind of pain is "ten times worse" than another, but I have always regarded this as a child's way of saying "much

* *Brit. J. of Psychol. (General Section)*, 23, 401-3 (1933).

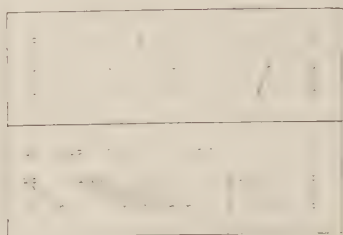
worse." To Dr Richardson the numbers apparently have a meaning, but to me the statement that a certain pain is ten times as intense as the one I am experiencing carries no precise significance. The conjunction of numbers and sensations may sometimes be merely a matter of mental association, comparable for example with the association formed by some people of the days of the week with particular colours. If I understand Dr Richardson correctly he claims to recognize ratios in sensations, but not to be able to recognize the intensity level of a single sensation. For example, in the paper referred to the scale is defined by taking α as 100, where α is "that pain which just prevents one from going to sleep at the time and under the circumstances in which one does ordinarily fall asleep when free from pain." A definition of this kind is not without its dangers: to take a somewhat analogous case concerning the sense of hearing, one may ordinarily not be awakened by a violent thunderstorm at the time and under the circumstances in which one is ordinarily awakened if one's name is spoken.

Mr Maxwell and Mr Bartlett appear to be concerned with the comparison of intervals or differences between sensations rather than ratios. Mr Maxwell refers to interpolation between standard sensations; but the sensations in fact are not standards, but merely the sensations resulting at the particular time from exposure to standard stimuli. Apparently Mr Maxwell does not rely on judgments of ratios of intensities, though for Dr Richardson these "ratios were estimated in a manner so direct as to elude analysis." If I may judge from my own trials and those of some of my colleagues who have made colour experiments on the lines proposed by Dr Richardson, the estimation of these ratios is commonly difficult and the process is both slow and indirect. Even though efforts were made to disregard any knowledge based on general experience of measurements, the results suggest that the numbers obtained were influenced by past experience where this existed. In general there are wide differences* from one person to another in the values reached as well as in the mental paths followed in obtaining them. I can therefore neither subscribe to the implications of Mr Maxwell's claim that the observer "knows his own mind" nor on the other hand attach importance to Mr Maxwell's mean curve, which is assumed to be a function solely of the form of the question and the answer given, and independent of the varying criteria adopted by different subjects.

My own trials lead me to think that in some of these investigations the number of arbitrarily fixed points is too small to define a scale. For example, in placing a pink on a scale bounded by white at one end and red at the other I may try to imagine the appearance of a coloured band which changes "uniformly" from white to red, and to place the pink strip at the appropriate position of the band. I then encounter the difficulty that "uniform" is so uncertainly presented to my imagination that a pink physically half-way between the white and the red may occupy any position in the central half of the linear interval, and may conceivably even lie outside it. If any position within this large fraction of the whole length is selected, there is no

* As far as I can judge the spread of the observed points in my experiments was distinctly greater than in those of Mr Maxwell. This appears to me to be largely a matter of chance; the spread is not necessarily of importance.

difficulty in placing additional colours of the white-red series with considerable precision to form what appears to the eye as a "uniformly" changing series. This experience may imply that the particular intervals white to pink and pink to red are dissimilar in type, so that there is no intrinsic meaning in their ratio: it suggests on the other hand that compound ratios invariant on projection may be of significance. The process is certainly very different from that involved in comparing two lengths.



The accompanying diagrams may be of interest. The isolated points of the top row in the upper diagram represent the positions assigned to colours by Richardson's method, the colours varying from red through yellow to yellowish green. The corresponding row of points in the lower diagram relates to a blue-green series of low luminosity. The bottom row of each diagram represents measurements of the stimuli. Three suitable members, representing approximately the extreme and the mean of the top scales, were used to determine a projection so that the positions of the three estimated points were moved to coincidence with the corresponding measured points. The projected points are shown on the middle line, and connections between measured and estimated points are added. In the upper diagram the two additional joins are approximately vertical, and suggest that the estimates are projectively related to the stimulus measurements*. The approximate parallelism of most of the joins in the lower diagram suggests that a similar relation holds here also, the points which happen to have been chosen for reference being the least regular. The irregularities, including the one reversal of order between measurement and estimate, are undoubtedly due to the disturbing effect of differences in luminosity, though these differences were not really great. These two examples certainly do not contradict Dr Campbell's conclusion that, however unconsciously, our numerical estimates relate to the stimulus. I ought to add that I have no experience of colorimetric measurements, so that the distribution of my points was not in any way influenced by a knowledge of what measurement would yield.

Dr J. H. SHAXBY. I am in general agreement with the views of Dr Campbell on these problems of sensory magnitudes. I confess that I have never been able to persuade myself that such an estimate as this of a pink, by placing a point on a line whose extremities represent red and white, is not an assessment of stimuli rather than of sensations. If I try to estimate a weight in the same way in relation to two

* It is pertinent to remark that different systems of colour scales are projectively related to one another.

other weights, one lighter and the other heavier, I seem to be asking myself what weight will produce the same sensation by interpolation between the sensations given by the two extreme weights, i.e. I am making a judgment of stimuli.

The particular stimulus in question in the red-pink-white test is not so obvious as in the matter of weights, but I cannot feel that there is any essential difference between the two cases.

In other words, I seem to be using my sensations as a sort of apparatus to form a scale of measurement of the stimuli producing those sensations. If I knew nothing of the experimental work on just-perceptible-differences, I should be tempted to call this scale a linear one, that is to associate equal lengths on it with equal changes in the stimuli. That this is not so seems only to indicate that my sensory apparatus gives "readings" related to the stimuli in a way more complicated than that of proportionality, and not to justify me in supposing that I am measuring something quite different, namely my sensations. I am no more establishing a scale of sensations than, in using the positions of the deflected pointer of a galvanometer, I establish a scale of angular measurement. Just as I assume this scale of degrees in using the galvanometer, so I assume a sensation scale as the indicator of gravitational or pinkness stimuli, and in the very act of doing this I rule out any possibility of finding out anything fundamental about the quantitative aspects of sensation. I have consciously or unconsciously made a definite, but unverifiable, assumption about my sensations, and, having done so, I may not argue back again to any law of magnitude of sensations.

In all such tests we use our memory of previous (even if immediately previous) sensations to make the very sort of test that Dr Campbell shows that we can make more sensitively by an actual variation of stimuli to produce a sensation not differing appreciably from the one experienced: a sort of null method.

Further there is the great difficulty of adaptation, which affects all our sensory estimates. Such methods as these under discussion not only leave the degree of adaptation out of account, but necessarily make its value indeterminate.

Incidentally, what sensations or stimuli are estimated in Dr Richardson's experiments? In the simplest way of conducting them one end of a line stands for maximum redness, the other for maximum whiteness, but also there is least brightness at the red end and greatest at the other. Are we then judging by redness, whiteness, redness versus whiteness (saturation), brightness, or a combination of these? It must surely be some combination, for if we made the brightnesses of the red and of the white (grey) each equal to that of the given pink, we should, I think, get a different position of the pink on the line. In other words, in marking a point on the red-white line we are attributing to a unique sensation a particular position on a scale, but this scale is not a function of any simple sensation or stimulus, and we have no means of knowing the parts played by different variables in fixing the scale.

Major J. L. P. MACNAIR. I think the controversy really goes a good deal deeper than any question of stimuli or sensations. Briefly it appears to me to resolve itself into the fundamental problem, about which psychologists are still by no means

agreed—have we a mind or not? If we have, *R* might represent some form of subjective measurement. If not, and all perception is purely physiological, then *S* is really the same thing as *R*, though there may be many intermediate steps.

But even in the latter case, to measure anything physically we must have something to measure it against. What? I do not find Richardson's analogy of the $\frac{1}{10}$ -centimetre guess convincing. When judging $\frac{1}{10}$ centimetre we are in reality making a mental comparison with a measuring rod whose form is very familiar to us.

Mental measurements, if really distinct from physical comparisons, must be absolute. But what is absolute mentally always turns out to be relative when looked at physically; see Dr Thouless's experiments on the projectional visual observation of an inclined ellipse. It is practically impossible to say at what stage an ellipse rotated about its minor axis projects a circle to the eyes, because the mental process takes into account the surrounding objects. Hence the very seeming inaccuracies complained of by Dr Campbell are in a way a support for mental theories. For this reason also orders of difference cannot, I think, possibly provide a method of approach.

The difficulty will not be finally resolved until we have decided whether mind is to be regarded as separate from body or not. At the same time the "philosopher in the street" (whom I diffidently claim to represent) must welcome Dr Campbell's interesting and provocative paper and the discussion it has aroused, as helping us towards such a decision.

Capt. C. W. HUME. Whenever by inadvertence I get into a hot bath with cold feet I always look at the thermometer. In the trying circumstances it is a great comfort to reflect that this latter is an instrument of precision whereas my mental estimate of the intensity of sensation is fallible if not meaningless. I just take the logarithm of the absolute temperature, and bear in mind that this is the only quantity that has assignable significance.

Dr J. O. IRWIN. I have been struck by the fact that there appears to be an analogy between a judgment of sensation and a judgment of probability. Probability is defined by Mr Keynes as the degree of rational belief in a proposition on certain evidence. Strictly speaking for given evidence there can only be one rational degree of belief in a proposition, but Mr Keynes admits that different people might differ in their degree of belief in a proposition on the same evidence. He says, for instance, "Some part of knowledge, knowledge of our own existence or of our own sensation, is clearly relative to individual experience. We cannot speak of knowledge absolutely—only of the knowledge of a particular person. Other parts of knowledge—knowledge of the axioms of logic, for example, may seem more objective. But we must admit, I think, that this too is relative to the constitution of the human mind and that the constitution of the human mind may vary in some degree from man to man. What is self-evident to me and what I really know, may only be a probable belief to you or may form no part of your rational beliefs at all. And this may be true, not only of such things as *my* existence but of some logical axioms also.... What we know, and what probability we can attribute to our rational beliefs, is therefore subjective

in the sense of being relative to the individual. But given the body of premises which our subjective powers and circumstances supply to us, and given the kinds of logical relations upon which arguments can be based and which we have the capacity to perceive, the conclusions which it is rational for us to draw stand to these premises in an objective and wholly logical relation."

For "degree of rational belief in a proposition on certain evidence" substitute "sensation evoked by a stimulus under certain conditions" and the analogy begins to appear. If we could make the conditions sufficiently precise it is difficult to believe that we should not get a unique sensation corresponding to a given stimulus, but in actual practice different people may differ in the sensation evoked by a given stimulus, or the same person may differ on different occasions.

It does not follow that the sensation is measurable any more than it follows that the probability is measurable. One may again quote Mr Keynes. "There are some pairs of probabilities between the members of which *no* comparison of magnitude is possible; that we can say, nevertheless, of some pairs of relations of probability that the one is greater and the other less, although it is not possible to measure the difference between them; and that in a very special type of case, to be dealt with later, a meaning can be given to a numerical comparison of magnitude." For "probability" substitute "sensation," and would anyone seriously quarrel with the statement? We may note in passing that of course probability in the sense of "degree of belief" is quite a different thing from "empirical frequency" or the relative number of times an event will happen in the long run, but again under some circumstances there will be an intimate connexion between the two.

The following extension of the analogy is perhaps no more than suggestive. If we write R for stimulus and dS for a small increment of sensation we might write

$$dS = f(R) dR,$$

meaning that the just perceptible difference in stimulus is some function of the stimulus increment*. Now dS , as Dr Campbell has shown us, does not measure sensation, but it may be related to it. Now suppose we are examining some measurement—say the stature of a few hundred or thousand individuals—let us write x for stature and dx for a small increment of stature: then we shall find $dp = \phi(x) dx$, where dp is the proportion of individuals whose stature lies between x and $x + dx$. Now dp is not a probability, it is an empirical frequency; but it is closely related to a probability. Is it too fanciful to suppose that dS is related to sensation as dp is related to probability? To complete the analogy we should have to be able to identify dp with the smallest difference in stature (x) such that for the two values x_1 and x_2 between which the difference lies one of the two propositions "the stature of this man is x_1 " and "the stature of this man is x_2 " could be judged more probable than the other. Is this legitimate? At any rate it raises the hope that some competent logician might be able to state precisely the conditions under which sensation would be a measurable quantity.

Again I can see no reason why keen experimentalists should not ask people to

* If $f(R) = c/R$ we have Weber's law.

make mental estimates or guesses of the point on a line which corresponds to the probability of a given proposition on given evidence, just as Dr Richardson has obtained mental estimates of colour-saturation, loudness and pain.

The Rev. R. S. MAXWELL. In his analogy with temperature in paragraphs 2 to 5 Dr Campbell appears to have begged the question with regard to the experiments conducted by Dr Richardson and myself. Throughout, we were concerned with the measurement of sensations, not of stimuli. The sensation of warmth is surely a different thing from temperature. It may be granted that any such measurement is in a very primitive stage and is not necessarily very accurate. The underlying question appears to be "Is it possible to make any such measurement quantitatively at all? I.e., can we assign any numerical value to such sensations as we may experience in terms of standard sensations—a standard sensation being defined as the sensation produced by a standard stimulus?"

I should be prepared to maintain that the answer to such a question is definitely in the affirmative. I have tried it myself in the case of colour estimations*, the loudness of sounds in a telephone receiver†, and the temperature-differences of water in various beakers. I feel that for myself I can assign a definite numerical value to such sensations. Call it guessing, if you will. No one would expect a very high degree of accuracy in the use of such a method, but I feel that what I measure is an internal sensation, and not an external stimulus.

Take the question of temperature-differences in more detail, since Dr Campbell refers to it especially. A few days ago I tried the following experiment. I took two beakers containing water at 25° and 35° C. respectively, and got an assistant to pour water of an unknown temperature into a third beaker. I placed the first finger of the right and left hands into the hot and cold water respectively. This gave me a standard sensation produced by a standard temperature-difference. After fifteen seconds I transferred the right hand into the beaker containing the water at the unknown temperature. This gave me the sensation due to an unknown temperature-difference, and I felt quite confident in assigning a numerical value to such a sensation, and although I should not be prepared to claim any high degree of accuracy for it, I definitely feel that it did represent a quantitative mental estimate of temperature-difference. When fourteen such estimates were made, the results, although somewhat scattered as might be expected for such a crude experiment, did lie more or less evenly distributed about a straight line.

One final suggestion. Is it possible that the whole controversy has arisen through a misunderstanding of the meaning of the words used by Dr Richardson and Dr Campbell? The quantitative mental estimates either of colour, or sound-intensity, or temperature-difference made by Dr Richardson and others do appear to have some perfectly definite meaning even if they do not conform to Dr Campbell's more rigorous definition of the word "measurement." Would it not be possible to use the word "estimate" rather than "measurement" in such cases? Dr Richardson

* R. S. Maxwell, *Brit. J. Psychol.* 20, 181-9 (1929).

† L. F. Richardson and J. S. Ross, *J. of General Psychol.* 3, 299-300 (1930).

himself appears to hint at some such course when he suggests that "Sensation belongs to some more primitive type of magnitude which has hitherto escaped classification"*.

Dr R. A. HOUSTOUN. It would help to clarify our ideas if Dr Campbell could answer the following questions on the subject of his paper. The visible stars have been divided into six magnitudes since the time of Ptolemy. For centuries the estimation was made visually, but now it can be done photometrically by comparing a star with the pole star or with an artificial star and altering its intensity by means of a nicol prism, or it can be done photographically by measuring the blackening of the image. The results obtained by the three methods can be related by formulae.

What did Ptolemy measure by his magnitudes, if it was not sensation? Is the term "measurement" to be withheld from the results obtained by the visual method and allowed to the results obtained by the other two methods?

Reply by Dr L. F. RICHARDSON:

1. Physicists are accustomed to estimate mentally, or if you prefer to guess, tenths of a scale division; also to guess tenths of a second when using a clock beating whole seconds. But let no one suppose that I advocate an extension of guessing in practical physics; for I really admire the growth of instrumental precision. The present controversy is not about physics but is about logic, psychology and metaphysics.

2. If anyone desires to read the theory of order and quantity set out with clarity and charm let me recommend *The Fundamental Concepts of Algebra and Geometry* by John Wesley Young†. Of course we must all agree with Dr Campbell that "a process of assigning numerals is not regarded as measurement unless it fulfils conditions more stringent than the mere representation of order." But mental estimation gives more than mere order. This is well known in connexion with estimating tenths of a scale-division. Again, if you saw an ordinary street of houses all alike numbered consecutively 1, 2, 3, 14, 25, 638, 639, would you not feel that although the order was correct the numbering was silly? Would you not feel this immediately without needing to measure distances with a tape? If so you become immediately aware of more than mere order. Dr Campbell admits this himself in regard to yellowness in his § 10 and indeed he proposes an ingenious difference-method for assigning numerals.

The serious question is not whether sensory events are quantitative, but how accurately they are quantitative. That can be found out by psychophysical experiment, but never by mere argument. Here follows a suggestion for a crucial experiment. Let four stimuli *A, B, C, D*, steadily increasing from *A* to *D* in some quality, be adjusted so that the successive intervals of sensation appear equal when the stimuli are considered in adjacent pairs, namely *AB* with *BC* and then *BC* with *CD*. How nearly does the interval of sensation from *B* to *D* then appear to be twice the interval of sensation from *A* to *B*? The accuracy of this result is known to be good

* L. F. Richardson, *Report on Vision*, pp. 112-14 (Physical Society, 1932).

† Macmillan, New York (1911).

when the sensation is that of lengths drawn on paper, but for loudness, colour, warmth, taste and pain there is I believe as yet very little definite information about accuracy in this sense, although there is already a good deal of information about accuracy of repetition of estimates of various sensations.

3. I disown the remarks of the fictitious Dr Richardson introduced by Dr Campbell in his § 3, and give instead my own conviction that the sensation of warmth is quite distinct from thermodynamic temperature. Similarly for colour. What should we think of a fictitious person who could not distinguish qualitatively between a wave-length and the sensation of colour which it produces?

4. Important in Dr Campbell's argument is his doctrine about the sameness of things. He uses the phrase "the same thing" at least ten times, and in a very peculiar and confusing sense. Thus in § 5 he states that "two methods measure the same thing, if the order of the numerals assigned by one to the members of a group is always the same as the order of the numerals assigned by the other to those same members." Because, as x increases, x^3 , $\tan^{-1} x$, $\exp x$ all steadily increase, therefore according to Dr Campbell, x , x^3 , $\tan^{-1} x$, $\exp x$ all measure "the same thing." Neither in mathematics nor in common speech is it customary to say that x and x^3 measure the same thing. This doctrine of Dr Campbell's is metaphysical and reminds one of Kant's doctrine of the alleged things-in-themselves behind phenomena. To prevent confusion we ought to have a technical term, and I propose in future to call Dr Campbell's "same thing" a "same N.R.C. thing."

I am now able to state that whereas sensation and stimulus are entirely distinct, yet under specially constant circumstances they are approximately the same N.R.C. thing.

5. A fundamental distinction between sensation and stimulus is that each person has his own immediate experience of sensation, but only an inferred and usually co-operative knowledge of stimuli. Hamlet's epigram on the certainty of immediate experience* may be crudely brought up to date as follows:

Doubt how electrons behave;
Doubt if anything really is there;
Doubt whether sound is a wave;
But never doubt you hear,

Unless of course you really *are* not quite certain.

This comic anticlimax supports the thesis, for "not-being-quite-certain" is a personal mental state, very different from a stimulus.

6. The plainest evidence that sensation is not, in ordinary parlance, the same thing as the stimulus external to the human body is afforded by a study of the illusions, Gestalt-phenomena†, eidetic images† and hallucinations. For example a sensation of brightness may be produced either by a train of waves entering the pupil or

* Act 2, Scene 2.

† E. R. Jaensch, *Eidetic Imagery* (Kegan Paul, London, 1930); W. Köhler, *Gestalt Psychology* (Bell & Sons, London, 1930).

by digital pressure on the outside of the eyeball. Now if the sensation is the same as each of these different stimuli, it would follow that the stimuli are the same, which is absurd. It may be replied that each kind of sensation is in one-to-one correspondence with a special state of affairs in the brain; but even so, a state of affairs in the brain is not what we mean ordinarily by the "stimulus".

7. With regard to the minor variations in the relation between stimulus and sensation, that is to say setting aside hallucinations and illusions of the more extreme kind and considering only such minor affairs as simultaneous and successive contrast, Dr Campbell gives two strangely different arguments. *Firstly*: when these minor variations are negligible, he regards this in his § 5 as evidence that a mental estimate of a sensation and the measure of a stimulus are the measures of the same N.R.C. thing. I agree, but find the statement rather dull. *Secondly*: when these minor variations are not negligible, Dr Campbell in his § 8 considers that the variations indicate that the mental estimate is not an estimate of a sensation. In other words he accuses the observers of not knowing their own minds. Most people know their own minds more or less, though not perfectly. Dr Campbell condemns the whole procedure because some of the details are unclear. I think it will be much wiser to go patiently on with the experimental elucidation of these variations.

In the last paragraph of his § 8 Dr Campbell attends to the chief difficulty of psychology, namely the privacy of the individual mind. It is indeed a formidable difficulty. Personally I refrain from assuming either of the criteria which he mentions and rejects. It is not convenient to have to remember the individual estimates of hundreds of observers; so I prefer instead to state their mean and their standard deviation. This is a harmless, customary and useful procedure and there is no justification for Dr Campbell's violent condemnatory words.

8. With regard to the functional relation between stimulus and the average of the estimates of sensation, the credit of obtaining the interesting curve, which Dr Campbell attributes to me, is really due to the Rev. R. S. Maxwell, B.Sc.

In discussing this curve Dr Campbell asserts in his § 7 that "Physicists do not regard a law as a true numerical law, unless its form is simple and/or explicable by a theory; if it does not fulfil that condition, it is a mere empirical law." This statement of Dr Campbell's contains, I think, more than one misleading antithesis. For the opposite to "true" is "false," not "empirical." Also the opposite to "simple" is "complicated," not "empirical." For example, Stefan's radiation law was in the year 1880 empirical and simple and true for black bodies, before its thermodynamic theory was published by Boltzmann in 1884. Again, the law by which the tides at any particular port are predicted is fairly true, decidedly complicated and partly empirical. Disagreeing as I do with Dr Campbell's fundamentals on laws, it is useless for me to argue about his deductions on this subject.

9. A restriction of the meaning of the word "measurement" so that it should apply only to what Dr Campbell has named A-magnitudes and B-magnitudes is recommended by several speakers. Such a conventional restriction might suitably be left to the decision of the Committee appointed by Sections A and J of the British

Association in 1932. But I must point out that Dr Campbell formulated his valuable classification of types of magnitude before he had sufficiently considered the existence and properties of mental estimates. Dr Houstoun in this Discussion has mentioned excellent reasons for not thus restricting the meaning of "measurement." Might we not suitably say that mental estimates are "C-magnitudes," and that all magnitudes are measured?

10. Taking each person's word "measurement" in his own sense, I am happy to be in general agreement with the remarks of Mr R. J. Bartlett, Dr W. D. Wright, Capt. Hume, the Rev. R. S. Maxwell and Dr Houstoun and am much interested in the facts brought into comparison by Dr Beatty.

11. As to bias, I agree with Mr Guild that experience of painting, dyeing or of colorimetry would be likely to distort mental estimates of colour. But ordinary adolescents should be much less biased.

12. Mr T. Smith has much to say about the difficulties experienced by himself and some colleagues and mentions by contrast the lesser scatter in the estimates of Mr Maxwell's schoolboys. But the existence of great learning and intelligence in some persons, who find difficulty in making estimates, does not, I think, discredit the estimates of those who make them easily. For among nearly 400 persons, whom I have asked to make estimates, there was no obvious connexion between refusal on the one part and learning and intelligence on the other. Also it is known that various sensory accomplishments are distributed among the population in a manner having no important correlation with general intelligence. According to G. M. Whipple's *Manual of Mental and Physical Tests** this is so for the discrimination of lifted weights and of double touch on the skin. Some very intelligent people are colour-blind, as John Dalton was. An honours B.Sc. is no guarantee that its possessor can sing in tune. Sometimes logical propensities are actually a disqualification. Thus Sir Francis Galton found that imagery was weaker among those accustomed to much abstract thought than among women and children†. Again Mr Dudley Heath of the Royal College of Art remarked, in connexion with estimates of pink, that those art-students who decline to make a decision in this and similar problems are those who are also argumentative; and that they could place the mark on the line if they would trust to their first impressions, instead of to reasoning‡.

Reply by Dr N. R. CAMPBELL:

1. To much of the discussion I can reply generally. I am not competent to discuss whether Dr Richardson's facts are indeed facts, or whether there are similar facts concerning other branches of sensation. In order to limit the issue I do not propose to discuss *here* whether other alleged methods of measuring sensations, e.g. the equal-interval method or the just-perceptible-difference method, are actually measurement. The opinions on these matters are interesting, but beyond my present scope. I am only asking whether Dr Richardson has produced evidence that his method measures sensations, on the assumption that his facts are facts.

* (Warwick & York, Baltimore).

† See W. James, *Principles of Psychology*, 2, 51-57.

‡ *Brit. J. Psych.*, General Section, 20, 36 (1929).

I maintain (in accordance with Mr Guild) that nothing but confusion and error can result from using "measurement" in any but its accepted sense. I call nothing measurement that does not possess the distinctive features of the processes physicists accept as measurement.

I do not deny a difference between sensations and stimuli, and I fully recognize that there are facts, beyond the scope of physics, well worthy of study. But to study is not necessarily to measure. Everything concerned in a process of measurement is not measured by that process—e.g. the colour of a titration indicator or the luminous flux from a galvanometer lamp. To say that two processes measure the same thing is not to deny that there are things, not measured by either of them, in which the processes differ.

2. I will start with Dr Richardson, considering only his main points not covered by paragraph 1.

Estimating tenths is measurement only because it has been shown to agree approximately with better ways of measuring the same thing. In so far as the estimates give a result different from that of the better methods, they are wrong; witness the term "decimal error." And here I may answer Dr Houstoun's question. Until the Ptolemaic method had been shown to agree with physical methods, there was no evidence that it measured anything; it was on a par with Mohs's scale of hardness. Now it has been shown to agree, it is simply a bad way of measuring something that is better measured otherwise. These two examples support, not undermine, my position.

I do not admit that the mathematician's "quantity" is the same as the physicists "quantity." Dr Richardson's citation of Dr Young's work shows well the danger of calling different things by the same name. I do not deny that mental estimates give more than order; but I do deny that they give enough more to constitute measurement. I accept his view that mental estimates are probably an indirect way of recognizing equal intervals; but the question remains whether measurement can be based on such recognition.

I maintain my position about "measuring the same thing", for Dr Richardson's evidence supports it. There are actually no two recognized physical magnitudes related as are x and x^3 , or as x and any other mathematical function of x having the same order; $\tan^{-1} x$ has not the same order. The reason is that, when we find ourselves measuring two quantities so related, we realize that they are the same and drop one of them. The nearest approach to the position Dr Richardson contemplates is when we recognize magnitudes (e.g. period and frequency) related as x and $1/x$ or $(1-x)$; but then the order is not the same; it is reversed.

I have not accused observers of not knowing their own minds. A man may know his own mind and yet be wrong. I do not deny that observers may associate particular numerals with particular sensations. I deny only that they have that kind of reason for the association which would make it measurement.

The context shows that I use "true" merely as the dictionary antithesis of "empirical" and not as the dictionary antithesis of "false."

3. In reply to Dr Beatty, Mr Bartlett, Capt. Hume: See paragraph 1.
4. In reply to Mr Guild: Any differences between us appear to me to be differences of emphasis or of expression rather than of substance. I do not know of any further criteria necessary for "measuring the same thing," but am prepared to admit that there may be some that I have overlooked. I should like to stress Mr Guild's statement that the *Rs* are complex functions of both sensations and stimuli.
5. In reply to Dr Wright: I agree that *if* a sensation is a magnitude, and *if* mental estimates measure it, *then* *R* and *S* are not the same thing. But I deny utterly that Dr Richardson has produced any evidence for either part of that hypothesis. The analogy with the basket of apples is incomplete. It would be complete if our estimate of the number of apples depended on whether the 8 apples had been put in the basket originally or whether they had been left after 4 had been taken away from an original 12. Neither Dr Wright nor anyone else meets the point (emphasized when I read the paper) that you must define what you mean by two observers having the same sensation before you combine their observations. Until that definition is given, all analogies with accepted statistical methods are misleading. Finally, see paragraph 12 below.
6. In reply to Mr Smith: I accept most readily his suggestion that mental numerical estimates can be analyzed into recognitions of non-numerical relations. I have some work on this matter in hand.
7. I agree entirely with Dr Shaxby, especially with his third paragraph.
8. In reply to Major Macnair: I have never been able to make up my mind whether I have a mind; I rather think not. But I seem able to interest myself in these discussions without one.
9. In reply to Dr Irwin: I accept entirely his view that there is an analogy—and a helpful analogy—between Keynes's probability (a function of belief) and sensations. But since I am not considering alleged measurement by means of just-perceptible differences, I will not examine his last paragraph.
10. In reply to Mr Maxwell: Surely it is he who begs the question. The question at issue is precisely whether we *are* concerned with measurement of sensations or of stimuli. The remainder of his remarks have already been dealt with implicitly.
11. I have already answered Dr Houstoun's question.
12. Finally, I have realized that there is a very serious error in the last section of my paper. I have there assumed that pairs of sensations similarly related are necessarily represented by pairs of numerals with constant arithmetical difference. This assumption is false; I have fallen headlong into a pit that has trapped many psychologists. I am dealing with the matter elsewhere. So if the method of differences there proposed is, as Dr Wright suggests, identical with the Weber-Fechner method, that method is not merely old, but also fallacious.

A METHOD OF MEASURING THE SPECIFIC HEATS OF POOR CONDUCTORS

By W. G. MARLEY, M.Sc.

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ABSTRACT. A brief review of existing methods of determining specific heats is given with reference to their suitability for poor conductors. The method of cooling, which has received scant attention in the past, is developed to afford an accurate and ready method. This is used to measure the specific heats of typical substances.

§ 1. INTRODUCTION

IN connexion with the calculation of heat flow in walls the need has been felt of a simple and rapid method of measuring the specific heats of materials commonly used in building, and the present research was conducted with a view to the development of such a method for routine work.

The measurement of the specific heats of poor conductors is a matter of peculiar difficulty. Such materials are sometimes light and bulky and frequently of a granular or fibrous nature. They are, moreover, generally porous and retain a considerable quantity of moisture, the amount of which greatly affects the thermal capacity.

In order that the determinations shall be of practical value it is necessary that they be made under conditions approaching those obtaining when the material is used for its normal purpose. It will be seen that this requirement prohibits the adoption of some of the usual methods of measurement, and it is therefore proposed, before describing the present work, to review briefly the customary methods.

§ 2. REVIEW OF AVAILABLE METHODS

The method of mixtures is probably the simplest and best known method of calorimetry, though perhaps not the most accurate. It is particularly convenient for determinations of mean specific heats over a range of temperature, but it has been found to be impracticable with substances of the type at present under consideration owing to the change in moisture content during preliminary heating and to the difficulty of obtaining uniformity of temperature throughout the specimen.

In the early days of calorimetry, when accurate temperature-determination was a problem, methods of thermal measurement based upon the change of state of a calorimetric substance were particularly valuable. Bunsen's ice calorimeter and Joly's steam calorimeter are classic examples of apparatus working on this principle, while Dewar has applied the method in measuring specific heats at very low temperatures, using liquefied gases as calorimetric substances.

As the determinations in the present work have to be made at normal tempera-

tures, Bunsen's ice calorimeter would seem suitable; but the difficulty of heating a poorly conducting specimen to a uniform temperature without modifying its water content still remains, and with the thermometers available nowadays the method seems to have little advantage over the method of mixtures, while the apparatus is far more complicated.

The facility with which electrical energy can be measured, conveyed, and suitably dissipated has led to the development of several methods of calorimetry incorporating electrical heating. With such a method the specific heat of water at various temperatures was determined by Callendar and Barnes to a high degree of accuracy and their work probably represents the summit of achievement in the difficult field of calorimetry. Despite the undoubted advantages of electrical methods, research in them has been confined almost entirely to liquids: the author of an article in Glazebrook's *Dictionary of Applied Physics* says ⁽¹⁾: "Very little work has been done on the determination of the specific heats of solid substances by the electrical method except for metals. The method, of course, lends itself admirably to the determination of the specific heats of good thermal conductors, but with poor conductors special devices must be adopted to ensure uniformity of temperature throughout the material under test."

A method of measuring the thermal capacities of heavy powders has recently been described ⁽²⁾ by J. H. Awbery and Ezer Griffiths. A measured quantity of energy is introduced electrically and the material is constantly stirred by a special form of stirrer, but no correction is applied for the heat generated in stirring. The temperature-rise is recorded by multiple thermocouples and the thermal capacity of the apparatus is determined from experiments with water.

Griffiths previously described ⁽³⁾ a more complicated apparatus which he used for the accurate measurement of the thermal capacity of materials used in cold-storage insulation. This comprises an adiabatic calorimeter and, in order to obtain uniformity of temperature, the substance is stirred by vanes in a revolving drum. A heating coil imparts a known quantity of energy to the system and a correction is applied for the heat produced in stirring. Loss of heat is reduced to negligible proportions by maintaining an electrically heated jacket always at the same temperature as the drum, and the ultimate temperature-rise affords a measure of the thermal capacity of the drum and its contents.

The maintenance of such an adiabatic condition is by no means easy, and without it a correction has to be applied to allow for the thermal exchange with the surroundings. It would seem possible to utilize this cooling correction as a measure of the thermal capacity of the calorimeter and contents, and experiments have been conducted to develop a method on these lines. The method of cooling has not been used in the past for poor conductors on account of the difficulty of obtaining uniformity of temperature throughout the specimen. Perfect uniformity, however, is not necessary, for initial irregularities tend to even out if the rate of cooling is small [see Appendix], leaving a definite temperature-distribution which persists: the cooling of the specimen is then regular throughout its mass and affords a measure of the thermal capacity.

§ 3. APPARATUS USED IN THE PRESENT WORK

In the present work the specimen is contained in a vacuum flask, 30 cm. deep and 5 cm. in internal diameter, which fits tightly in a metal cylinder immersed in a bath maintained at constant temperature by melting ice (figure 1). The small annular space between the flask and cylinder is filled with water to ensure good thermal contact, and the specimen occupies the flask to a definite level (3.5 cm. from the top) which is conveniently found with a small gauge. A thermometer in the specimen enables the rate of cooling to be determined.

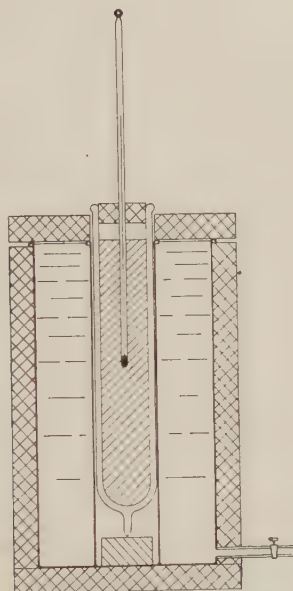


Figure 1. Section of apparatus.

Preliminary experiments with the flask indicated that the rate of transfer of heat was less than 0.003 calorie per second for a difference of temperature of 1°C . between inside and outside, and it was clear that the cooling would be so small that, even with a poor conductor in the flask, temperature-irregularities would vanish after a reasonable time.

§ 4. RADIAL VARIATION OF TEMPERATURE

If the mean temperature of a uniform circular cylinder, cooling slowly by radial flow of heat, is required, it may be found by measurement of the temperature at a point distant $1/\sqrt{2}$ of the radius from the axis. As will be seen in a later section, it is not necessary in the present instance to measure the mean temperature: all parts of the cylinder cool in the same substantially exponential manner, and it suffices to determine the rate of cooling at any one point, preferably in the axis of the cylinder.

§ 5. VERTICAL SURVEY OF TEMPERATURE

By means of a pair of thermocouples, one of which was situated at one particular point in the flask whilst the other was withdrawn along the axis in stages, the vertical variation of temperature was investigated for various sets of external conditions.

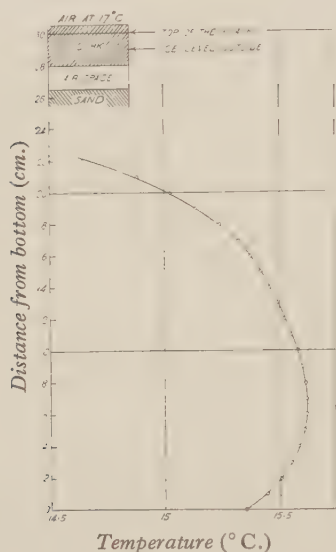


Figure 2. First vertical survey of temperature.

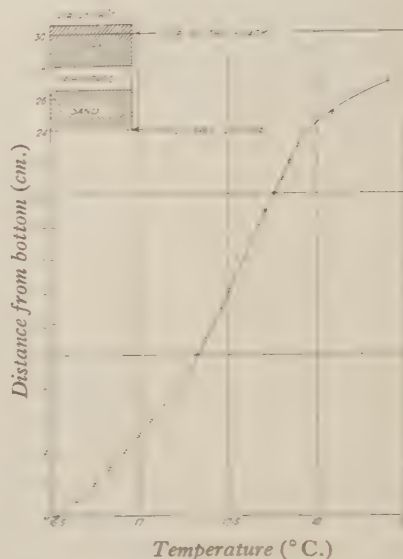


Figure 3. Second vertical survey of temperature.

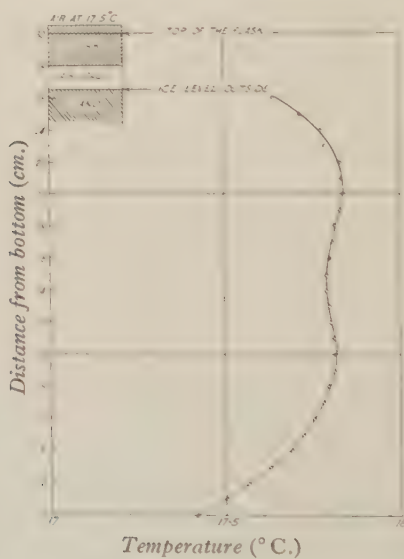


Figure 4. Third vertical survey of temperature.

In the first experiments the flask projected 1 cm. from the top of the ice jacket, whilst the level of the material (sand) inside was some 3.5 cm. below the top of the flask. The temperature was found to vary as shown in figure 2, from which it will be seen that excessive cooling is recorded near the top of the flask.

A second survey was then performed with the flask projecting a further 5 cm. above the ice jacket and the results, shown in figure 3, then indicated that the optimum position has been passed. The discontinuity in the curve at the level corresponding to the top of the ice jacket suggested that the level of the material in the flask ought to be the same as that of the cooling-bath outside. A third survey adequately confirmed this conclusion, and the vertical temperature-variation is seen in figure 4 to be almost zero in the middle section of the flask. In all subsequent work the flask was filled to 3.5 cm. from the top and immersed in the ice jacket to this level.

§ 6. EFFECT OF VARIATIONS IN LABORATORY-TEMPERATURE

Since 3.5 cm. of flask as well as the cork stopper are exposed to the air of the laboratory, variations in the room-temperature may influence the cooling appreciably. Experiments were conducted to investigate this effect, and two cooling curves were obtained under identical conditions except that the laboratory-temperatures were different. When these curves were plotted on a logarithmic scale of temperature, the rate of cooling was seen to be increased by a definite amount, 1.5 per cent, for every degree by which the flask-temperature exceeded that of the room, and when the curves were replotted with the time intervals between successive points increased in this proportion they yielded parallel straight lines. If the temperature of the flask is $\theta^\circ \text{C.}$ and that of the laboratory $T^\circ \text{C.}$, and if t is the time in seconds, it was found that $\delta t / \delta (\log \theta) = 1650$ when $\theta = T = 13$ and also when $\theta = T = 17$; but when $\theta = 17$ and $T = 12.9$, then $\delta t / \delta (\log \theta) = 1555$. Thus

θ, T, t

$$\delta t [1 + 0.015 (\theta - T)] / \delta \log \theta = 1650$$

in all three cases.

§ 7. INTERPRETATION OF RESULTS

From experiments such as that just described it was concluded that the curve obtained by plotting the logarithm of temperature against time, after correcting for variations in laboratory-temperature, was practically straight. This is very convenient, for in interpreting the result it is a simple matter to draw a good straight line through the plotted points and so minimize the effect of small errors in individual observations.

With the flask used in the present work the loss of heat amounts to some 160 calories per hour when the temperature-difference between inside and outside is 18°C. : this is lost almost entirely by radiation. A small quantity, not exceeding 10 per cent, is conducted along the glass wall of the flask, and a similar amount is probably transmitted by "carriage"* by the molecules in the residual gas of the

* W. Crookes, *Proc. R. S.* 31, 239 (1880).

vacuum. It seems not unreasonable to suppose that over a limited range of temperature the cooling is according to Newton's law. In this case the slope $\delta t/\delta (\log \theta)$ of the line obtained is proportional to M , the thermal capacity of the flask and contents, because

$$-M d\theta/dt = k\theta$$

and so, by integration,

$$-M \left[\log_e \theta \right]_{\theta_1}^{\theta_2} = k \left[t \right]_{t_1}^{t_2},$$

that is

$$M = K \delta t/\delta (\log_{10} \theta).$$

In this equation the constant K is a function of the flask alone, and the accurate evaluation of this quantity is an important part of the research.

Since values of $\delta t/\delta (\log \theta)$ are proportional to thermal capacities, they may be added and subtracted in like manner. Calculation is thereby simplified when, for example, the thermal capacity of the flask and thermometer is to be eliminated.

§ 8. METHODS OF MEASURING TEMPERATURE

Since the purpose of the research is to produce not only an accurate but a ready method of measuring specific heat, the method of determining the rate of cooling must be simple. Despite its extremely high accuracy the resistance thermometer is unsuitable as it requires complicated apparatus and has considerable thermal capacity which is a serious disadvantage.

From a thermal point of view a thermocouple is eminently suitable, but it needs an accurate potentiometer. Two pairs of couples were cemented to the flask, and in many experiments readings were made both with these and with an ordinary mercury-in-glass thermometer. The logarithmic cooling curve obtained by measuring the wall-temperature was parallel to that obtained from a mercury thermometer situated in the material at the same level, but the spread of the points was much greater.

The thermal capacity of the mercury thermometer and the fact that heat may be conducted appreciably along the stem may perhaps be cited as possible disadvantages, but the former is not serious in magnitude and the latter vanishes when the observations are corrected for variations in laboratory-temperature. The mercury-in-glass thermometer appears to be the most suitable instrument and was used in obtaining the results given later in this paper.

§ 9. CALIBRATION OF THE APPARATUS

The value of a method of calorimetry is greater if it can be used for absolute determinations. Very few methods, however, permit of this, and consequently the specific heats of most bodies are measured by comparison with a substance of which the thermal capacity is accurately known. With the present apparatus an attempt was made to balance the loss of heat by supplying electrical energy uniformly distributed

in the substance, but was abandoned as it was found difficult to maintain steady conditions for the long time necessary for the attainment of thermal equilibrium.

The most accurate comparisons are made when the physical properties of the substances compared are nearly the same, and the possibility of calibrating the present apparatus with solid materials was considered. There are, however, very few solids of which the specific heat is accurately known: the authors of the section dealing with the specific heats of elements in the *International Critical Tables* say ⁽⁴⁾: "... specific heat data on metals are rarely accurate to better than 1 per cent, an uncertainty of several per cent being not unusual."

An examination of the results obtained by various investigators ⁽⁵⁾ for the specific heats of otherwise suitable non-metallic substances reveals similar discrepancies of the order of 2 or 3 per cent. It is not a very satisfactory calibration which relies upon such results or even upon a probable value obtained from them.

The specific heat of water is known to a high degree of accuracy and the material is otherwise pre-eminently suitable as a standard. The first calibration was therefore made with the flask containing 542.8 gm. of water and a logarithmic cooling curve, the slope (8380) of which was proportional to the thermal capacity of the water, flask and thermometer, was obtained. In order to eliminate the thermal capacity of the flask and thermometer another curve, of slope 328, was obtained with the flask empty and, as is explained in § 7, the difference (8052) between the slopes corresponded to the difference between the thermal capacities (that is, to the known thermal capacity of the water) yielding a value 0.0674 for the constant K .

In order to obtain consistent results for the empty flask the preliminary heating was performed with the flask full of warm sand, and the thermometer in position; the sand was poured away and the flask quickly corked and inserted in the ice-bath. In the experiments with water the flask was filled to the standard depth given by the small gauge, and the readings were not commenced till two hours had elapsed from the start*, in order that steady conditions might prevail. The curves obtained were corrected for the effects of variation in laboratory-temperature (§ 6) and the slopes were measured at the point corresponding to 18° C. At this temperature the specific heat of water is 0.999 mean cal./gm.

It was thought that convection currents in water might possibly influence the results, and experiments were made to determine whether this was the case. It was found that the flask containing 550 cm.³ of coarse sand would also absorb some 220 cm.³ of water, and cooling curves were therefore obtained first with the sand alone and secondly with the same sand containing water: the difference between the slopes of the logarithmic curves corresponded to the thermal capacity of the water and yielded a value for the constant K . This experiment was repeated with a different sample of sand and again with fine copper turnings: the various values obtained for the constant are shown in table 1.

In these experiments any convection currents would be greatly reduced by the sand or copper turnings. The fact that the values of K obtained are in excellent

* This procedure was adopted with all the substances studied.

agreement with that obtained with water alone indicates that no error is being introduced by convection currents; the apparatus is therefore suitable for the determination of the thermal capacities of liquids.

Table 1. Experiments to confirm the calibration

Experiment	Material	Slope $\delta t / \delta (\log \theta)$ (minutes, °C.)	Constant K
3	856.2 gm. sand and 225.1 gm. water in flask	5940	0.0671
4	856.2 gm. sand in flask	2587	
(by difference)	225.1 gm. water alone	3353	
5	838 gm. sand and 220.8 gm. water in flask	5979	0.0669
6	838 gm. sand in flask	2675	
(by difference)	220.8 gm. water alone	3304	
7	1287 gm. copper turnings and 363 gm. water in flask	7440	0.0675
8	1287 gm. copper turnings in flask	2062	
(by difference)	363 gm. water alone	5378	

§ 10. TYPICAL RESULTS

The specific heats of some representative substances have been determined by observation of their cooling in the vacuum flask and the values obtained are shown in table 2.

Table 2. Specific heats of typical substances

Substance	Moisture content (per cent)	Measured specific heat at 18° C. (cal./gm.)
Copper turnings	0.0	0.090 ₉
Benzene	0.0	0.41 ₇
Potassium chloride	0.1	0.17 ₁
" "	0.1	0.17 ₃
" "	0.1	0.17 ₂
Sodium chloride	0.0	0.20 ₉
Cotton wool	3.3	0.30 ₄
Charcoal	4.5	0.27 ₇
Granulated cork	2.4	0.38 ₁

In order that the value of the present method may be more easily assessed table 3, showing results recently obtained by various observers for the materials listed in table 2, is given.

§ 11. ADVANTAGES OF THE METHOD

It will be observed that the range of the values given in table 3 is very large, especially in the case of poor conductors. As this is no doubt due to the difficulties of measurement, it is noteworthy that the present method is as simple and accurate when used with these materials as with good conductors such as copper. The

accuracy of the method may be judged to some extent by the consistency of results such as those shown in table 1 for water and the three separate determinations shown in table 2 for a sample of potassium chloride.

Table 3. Specific heats found by various observers

Material	Specific heat	Temperature (° C.)	Observer and reference
Copper	0.094	19	Kolossowsky, <i>Krak. Anz.</i> p. 596 (1912)
	0.0911	17	Nernst and Lindemann, <i>Berl. Sitzber.</i> p. 1160 (1912)
	0.0909	0 }	E. H. and E. Griffiths, <i>Proc. R. S. A.</i>
	0.0923	23 }	88 , 549 (1913); <i>Phil. Trans. A</i> , 213 , 119 (1913)
	0.0915	20	Harpur, <i>J. Wash. Ac.</i> 4 , 489 (1914); <i>Bull. Bur. Stand.</i> 11 , 259 (1915)
Benzene	0.414	7	Huffman, Parks and Daniels, <i>J. Am. Chem. Soc.</i> 52 , 1549 (1930)
	0.4078	20	Williams and Daniels, <i>J. Am. Chem. Soc.</i> 47 , 1490-1503 (1925)
	0.416	20	Dejardin, <i>Ann. Phys.</i> (9), 11 , 253 (1919)
	0.410	20	Tréhin, <i>Ann. Phys.</i> (9), 15 , 246 (1921)
Cotton-wool	0.319	—	Dietz, <i>Lpz. Monatsh. f. Textilind.</i> 27 , 85 (1912)
	0.362	0 to 100	Ottolenghi, <i>Mem. di Turino</i> (2), 57 , 97 (1907)
	0.280- } 0.283 }	0 to 34	Meltzer, <i>Dr. Dissert.</i> , Darmstadt (1928)
Charcoal, 6.89 per cent water	0.299	25	Griffiths, <i>Proc. Phys. Soc.</i> 33 , 335-361 (1921)
Granulated cork, 3.45 per cent water	0.438	25	Griffiths, <i>Proc. Phys. Soc.</i> 33 , 335-361 (1921)
Sodium chloride	0.2146	0	R. Weber, <i>Séanc. Soc. Neuchâtel</i> , 28 Marz. 1895; <i>Arch. sc. Phys.</i> (3), 33 , 590 (1895)
	0.2036	0 to 19.6	Brönsted, <i>Z. Elch.</i> 20 , 554 (1914)
	0.2078	24	Russell, <i>Phys. Z.</i> 13 , 59 (1912)
	0.2069	17 to 99	Magnus, <i>Phys. Z.</i> 14 , 5 (1913)
Potassium chloride	0.1652	58	Nernst and Lindemann, <i>Berl. Sitzber.</i> p. 1160 (1912)
	0.1616	0 to 19.6	Brönsted, <i>Z. Elch.</i> 20 , 554 (1914)
	0.1661	23	Russell, <i>Phys. Z.</i> 13 , 59 (1912)
	0.1654	16 to 99	Magnus, <i>Phys. Z.</i> 14 , 5 (1913)

With an ordinary mercury thermometer graduated in tenths of degrees the accuracy of reading is such that the plotted points are well aligned, and experience has shown that the slope of the line through the points can be determined within about 0.5 per cent. As the results are generally calculated from the difference between two experiments the ultimate error should be less than 1 per cent, and a comparison of the results quoted in tables 2 and 3 would tend to confirm this. Moreover with poor conductors such as sodium chloride the agreement is no less than in the case

of copper, and it is concluded that the accuracy is not greatly dependent upon the thermal capacity or the conductivity of the material. The method is therefore submitted as an accurate and ready method of measuring at laboratory-temperatures the specific heats of liquids and granular or fibrous materials of low conductivity. It is possible that the method could be extended to permit the determination of specific heats at other temperatures; for measurements in the neighbourhood of 100°C. , for instance, a steam jacket round the flask would be convenient. Such work, however, is somewhat outside the scope of the present research, which is confined to measurements at normal temperatures.

§ 12. ACKNOWLEDGMENT

In conclusion, the author wishes to thank Mr A. F. Dufton, of the Building Research Station, for suggesting the method and for his valuable encouragement and advice.

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- (2) *Proc. Phys. Soc.* **42**, 71, 232 (1930).
- (3) *Proc. Phys. Soc.* **33**, 355 (1921).
- (4) *International Critical Tables*, **5**, 92 (1st edition, 1929).
- (5) Landolt-Börnstein. *Physikalisch-Chemische Tabellen*, **2**, 1252 (5th edition, 1923).

APPENDIX. THE DECAY OF TEMPERATURE-IRREGULARITIES

c In a completely heat-insulated cylinder of length c , if the temperature be uniform over any plane at right angles to the axis and the initial temperature-distribution be of the form

$$A, p, x \quad \theta = A \sin \frac{p\pi x}{c},$$

t then, after time t , the temperature at the mid-point of the cylinder will be

$$a \quad \theta_t = A \left\{ \frac{2}{p\pi} - \sum_{n=1}^{\infty} \frac{4p}{\pi (4n^2 - p^2)} \cdot \cos n\pi \cdot e^{-4\pi^2 a^2 n^2 t / c^2} \right\},$$

when p is odd and a^2 is the diffusivity. From this formula values of $(\theta_t - \theta_{\infty})$ were calculated for a cylinder of granulated cork, for which $a^2 = 0.0032$ c.g.s.u. The values of $(\theta_t - \theta_{\infty})$ for an extreme initial variation of 1°C. are shown in the table.

p	$(\theta_t - \theta_{\infty})$ $t = 2 \text{ hr.}$	$(\theta_t - \theta_{\infty})$ $t = 3 \text{ hr.}$	$(\theta_2 \text{ hr.} - \theta_3 \text{ hr.})$
1	+ 0.099	+ 0.048	+ 0.051
3	- 0.089	- 0.043	- 0.046
5	- 0.035	- 0.017	- 0.018
7	- 0.023	- 0.011	- 0.012

With the experimental procedure described in the paper, observations of cooling throughout the third hour would be in error by the amount shown in the last column, an error of the order of 1 per cent when p is unity. It is clear that the error decreases as p (the number of peaks) increases and, furthermore, when the number of peaks is even the error becomes zero.

Since the radius of the flask is only one-tenth of the length, any radial irregularities of temperature will disappear long before the axial variations become insignificant, and a detailed investigation of these is therefore unnecessary.

By adequate mixing of the material the initial irregularities can be kept down to 1°C . The error, therefore, is likely to be very small and can be still further reduced by taking a mean of two or more experiments. It remains to point out that in the present research observations were not made till the third hour, and in most instances two or more curves which gave results in very close agreement were obtained.

DISCUSSION

MR W. C. S. PHILLIPS. I am particularly interested in this method of measuring specific heat as applied to poor conductors and insulators. The author has taken care to arrange conditions so as to obtain a uniform axial temperature near the middle of the flask, but I should be glad to know to what extent the radial variation in temperature is uniform. What method was adopted for initially heating the materials? If the initial temperature-distribution is very irregular after such heating, was it necessary to allow some time to elapse before taking readings of the thermometer?

MR J. H. AWBERY said that some thermometers would read a falling temperature correctly if tapped. The author's experience was not unique in this respect, but whether a thermometer behaved thus or not was a matter of luck.

AUTHOR'S reply. In reply to Mr Phillips: I would refer to §§ 4, 9, in which I have pointed out that, when the specimen is cooling exponentially, the position of the temperature-measuring device does not affect the slope of the logarithmic cooling curve obtained, although there may be a considerable drop in the temperature along a radius, amounting in some instances to one or two degrees. Slight heating was necessary to raise the initial temperature of the specimen a few degrees above that of the laboratory. This was done in a metal box while the specimen was stirred continuously, and it was found possible to keep the variations in temperature down to within 1°C . No observations were made till the cooling had proceeded for at least two hours (see § 9), and it is shown in the appendix that initial irregularities will then have become insignificant.

With regard to Mr Awbery's remarks I would like to say that I have used two thermometers in this work and both have been beyond reproach in the matter of freedom from sticking: this could be seen to some extent in the excellent alignment of the points on the cooling curves.

THERMOMAGNETIC HYSTERESIS IN STEEL

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ABSTRACT. The temperature variation of a new hysteresis of the thermomagnetic electromotive force in a steel wire is described. The hysteresis is of a negative or abnormal form, with a maximum amplitude of about $2 \mu\text{V.}$ between up and down branches. The accuracy of the apparatus and method is critically examined, and an error of more than $0.5 \mu\text{V.}$ in any reading is considered to be unlikely.

A qualitative explanation of the phenomenon is given in terms of Gerlach's* theory of spontaneous magnetization, and Broili's† results for nickel are discussed from the point of view of that theory.

1. INTRODUCTION

SEVERAL papers have recently been published describing the thermomagnetic e.m.f. in nickel and iron wires, and a hysteresis of the effect has been discovered for both metals. Band and T'ao announced‡ a hysteresis of the e.m.f. in iron, but described no detailed properties of the phenomenon. After the present work had been commenced, Heinz Broili§ described the temperature variation of the hysteresis of a similar e.m.f. in pure nickel wires. The nickel hysteresis was a normal type with small retentivity and coercive field, but the iron curve was peculiar in that a permanent remanent e.m.f., which never disappeared during several cycles, seemed to have been produced by the field.

Unfortunately the curve published by Band and T'ao showed signs of a vagrant shift of zero e.m.f. during the cycle, and there was not much detailed investigation into this source of error. The results given in the present paper were obtained with apparatus similar to that used previously in these laboratories, and appear to have established the hysteresis on a more secure basis. The results are numerous and the various sources of error have been traced out carefully until a satisfactory self-consistency has been attained.

The experimental arrangement used in the present work is similar in principle with that used by Sir William Thomson|| when the longitudinal thermomagnetic e.m.f. was first discovered. That used by Broili was different in that a uniform tem-

* Becker, *Z. f. Phys.* **62**, 253; **63**, 660 (1930); Gerlach, *Ann. d. Phys.* **8**, 649 (1931).

† Heinz Broili, *Ann. d. Phys.* **14**, 3 (1932).

‡ *Proc. Phys. Soc.* **44**, 166 (March, 1932).

§ Heinz Broili, *Ann. d. Phys.* **14**, 3 (1932).

|| *Math. and Phys. Papers*, **2**, 267-307.

perature is maintained throughout each part of the specimen wire over which a non-uniform magnetic field exists. Broili's apparatus gave the pure longitudinal effect, and we should expect the present results to be somewhat more complex though not beyond analysis. In the present work the potential leads (of the same material as the sample) were taken transversely to the field through small holes in the solenoid and were thus non-uniformly magnetized by the field even though they were not uniform in temperature.

2. ACCURACY OF THE APPARATUS

A water-cooled solenoid of the Moullevigen* form gave fields up to 380 G. uniform to 0.1 per cent over a length of 40 cm. A heating coil of nichrome wire wound non-inductively gave temperatures up to 900° C. uniform over 20 cm. and controllable to within 0.4° C. A water-cooling jacket, also in the axis of the solenoid, gave uniform cool temperatures over 20 cm. which were found to remain constant within 0.1° C. for periods of one hour†. Transverse leads of the same material as

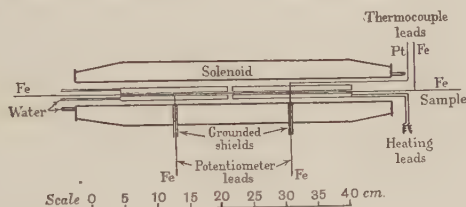


Figure 1. Section through the water-cooled solenoid, heating-coil and water-jacket. The Dewar flasks, potentiometer, galvanometer, etc., are omitted.

the longitudinal wire were taken out from the centres of these two uniform-temperature stretches and led through the solenoid into two Dewar flasks containing melting ice, where junction with the copper leads was effected. A Leeds Northrupp K-type potentiometer measured the e.m.f. between these two leads to within $0.5 \mu\text{V}$., against a standard cell placed in a thermostat maintaining a constant temperature to within 0.01° C. The last change in temperature would involve a change in the standard voltage of $0.406 \mu\text{V}$. The temperature of the hot part was measured by means of an iron-platinum couple, of which the iron element was the part of the sample projecting from the hot oven through the end of the solenoid, figure 1. In every case the wire was kept under constant tension by the application of a weight of 2 kg.

After the work had been completed we realized that errors might have been introduced into the temperature-measurements by the magnetization of one of the thermo-elements. In our case iron—the specimen itself—was used against platinum. If the temperature of the iron element varied appreciably in a strong field the thermomagnetic e.m.f. would be produced in the thermocouple, and only $0.2 \mu\text{V}$. would in our case be required to produce an error of 1° C.

* *J. d. Phys.* 7, 466 (1898).

† The water is obtained directly from an artesian well of considerable depth on the university campus, and its temperature is therefore almost independent of daily variations in surface temperatures.

A very searching test was therefore carried out to check this error. The iron wire was stretched as before down the axis of the solenoid and a piece of platinum wire soldered on at the centre of the heating coil. Another platinum wire and a copper wire were also attached at the same point to form an independent non-magnetic thermocouple to test for variations of temperature. Tests were then made over a complete cycle of the solenoid field at three different temperatures near 160° , 500° and 900° C. respectively. The reading of the platinum-iron junction was kept constant by adjustment of the heating current, and any variations in the other couple were noted. Variations of temperature of 1° C. could easily have been detected in the galvanometer reading, but no trace was found in fact at any of the temperatures. Even sudden changes in the field produced no detectable changes as between the readings of the two thermocouples, which were connected to two independent galvanometers of similar sensitivity.

We can explain this null result rather easily in our case. The iron element was kept at a uniform temperature throughout the strong part of the field, and not until the field is smaller does the temperature begin to vary; the e.m.f. produced must therefore have been less than that necessary to cause an error of 1° C. in the temperature reading. This error was found by test to correspond to less than $0.5 \mu\text{V}$. in the thermomagnetic e.m.f. measured in the potentiometer.

Had there been an error in the measured temperatures of about 5° C. due to the magnetic field, a spurious hysteresis phenomenon would have occurred: in maintaining the thermocouple reading constant the temperature would have been taken through a cycle during the field cycle, and the thermomagnetic e.m.f. values obtained would not have been those corresponding to some one temperature-difference between hot and cold ends; there would have been variable errors amounting to the order of several microvolts. It thus seems that accuracy to less than 1° C. is desirable for the temperatures at both ends of the specimen, and that this accuracy is actually attained in the present work.

3. RESULTS

Analysis of iron sample. The wire investigated in these experiments was thermoelement metal manufactured by the Kahlbaum Company. The diameter was uniformly 0.57 mm. Two independent chemical analyses showed that the metal contained only 98.97 per cent of iron, the remaining 1.03 per cent being chiefly composed of carbon, manganese and sulphur, with traces of silicon and phosphorus: the latter were not exactly determined.

The ordinary hysteresis properties of the wire were determined by standard methods. It showed magnetic saturation under fields of 75 G. at 23° C.; the intensity of magnetization being 1110 c.g.s. units. There was retentivity of about 77 per cent. At 275° C. saturation was reached in fields of 30 G., the intensity of magnetization being 740 c.g.s. units; and there was retentivity of 44 per cent. The coercive field necessary to reduce magnetization to zero after saturation was 15 G. at 23° C. and about 4 G. at 275° C.

At a later stage we hope to investigate the various related properties of the same specimen; magnetic resistance-change, specific-heat changes with magnetization, etc.

Hysteresis of the e.m.f. Figure 2 shows the hysteresis curves obtained when the hot end of the wire was at the temperatures respectively of 190° , 360° and 710° C.; in each case the cold end was between 19° and 20° C. The e.m.f. has been recorded as positive when it is directed from the hot end to the cold end of the specimen.

The initial e.m.f. in zero field was found in general to be about the same for any given temperatures after separate demagnetization processes. But sometimes it would differ by considerable amounts, even changing sign. Normally the initial e.m.f. would be positive from hot to cold end, but sometimes it would be in the opposite

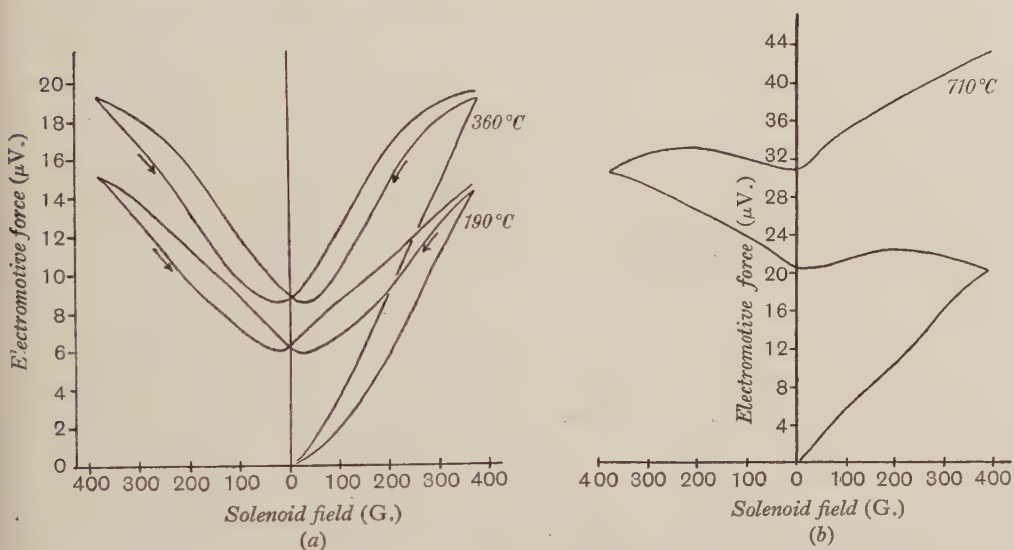


Figure 2. (a) Hysteresis of the thermomagnetic e.m.f., with the cold end of the wire at 19.5° C. and the hot end at 190° and 360° C. (b) Hysteresis with the cold end at 18.5° C. and the hot end at 710° C.

sense. This was probably due to incomplete demagnetization, as will be pointed out later in the discussion of the results. But the general form of the hysteresis was found to be independent of this initial discrepancy. A sample curve obtained when the initial e.m.f. was negative is shown in figure 4. After the first quarter-cycle there is not much difference from the curves of figure 2(a).

Effect of the transverse leads. To estimate the effect of the transverse leads on the hysteresis the longitudinal steel wire was removed and in its place a copper wire was stretched along the axis of the solenoid; the same steel leads to the potentiometer being used as before. The e.m.f. produced by the field was then determined as before. It may be permissible to subtract the e.m.f. found in this way from the total e.m.f. found before, and to call the difference the pure longitudinal e.m.f.; but this procedure seems to require too many assumptions to be rigorous. At least it gives us a qualitative idea of the facts, however.

Figure 3 shows the cycles obtained for two temperatures, respectively 200° and 350° C. at the hot end and 17.5° C. at the cold end in both curves. It will be immediately noted that there is no trace of a hysteresis loop, but that the field definitely introduces a permanent remanent e.m.f., which remains constant after the first quarter-cycle. This remanent e.m.f. remains constant throughout the field cycle. It increases with temperature, but not quite as rapidly as the remanent e.m.f.

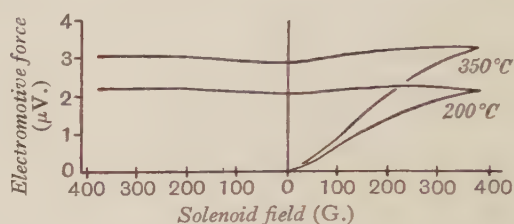


Figure 3. Complete cycles of e.m.f. in transverse leads, with the cold end at 17.5° C., and the hot end at 200° and 350° C.

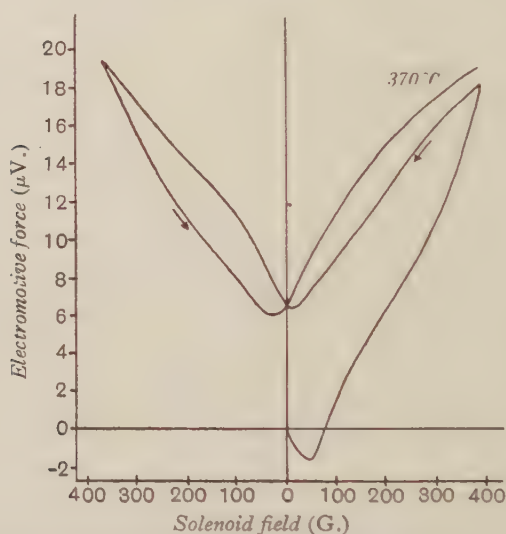


Figure 4. Hysteresis of the thermomagnetic e.m.f., when the initial e.m.f. in zero field is negative. Cold end at 22.5° C. and hot end at 370° C.

found in the total e.m.f., figure 2(a). We may therefore assume that the permanent remanent e.m.f. is due partly, if not entirely, to the transverse leads, while the hysteresis loop is purely a longitudinal effect.

Obviously it is desirable to perform the experiments without having any transverse leads, and some new apparatus designed for this purpose has already been constructed. The results will be published in another paper, because the principle of the arrangement is quite different from the present one.

4. DISCUSSION OF RESULTS

The theory of spontaneous magnetization. Although there is still a great deal of confusion in the literature between the idea of intrinsic field and that of spontaneous magnetization, the particular interpretation of the latter given by Becker* will serve to give at least a qualitative explanation of our hysteresis curves. According to Becker, two distinct phenomena occur when a metal undergoes ferromagnetization: (a) the reversal process in which magnetic vectors directed originally opposite (or nearly so) to the external field are suddenly reversed in sense without change of direction; and (b) the turning process in which vectors nearly parallel to the field are turned more nearly parallel. The latter process is supposed by Becker to be effective for magnetic resistance-decrease and magnetostriction phenomena, and by Broili† for thermomagnetic phenomena; but the reversal process is not supposed to have any influence at all in this respect.

Gerlach‡ considers that the turning process is essentially a change of the spontaneous magnetization (or true magnetization); and in order to account for the various phenomena connected with resistance change near the Curie point he assumes that this change in spontaneous magnetization is more easily effected by any given field when the temperature is increased towards the Curie-point value. Applying this idea to the present problem, we see that there should be a greater true magnetization (a greater change in the spontaneous magnetization) at the hot end of the specimen than at the cold end. The e.m.f. observed is then directed from parts of higher spontaneous magnetization to parts of lower spontaneous magnetization.

If now we further make the plausible assumption that at the colder temperatures there will be some hysteresis of the change in spontaneous magnetization, whereas at the hot end no such (or less) hysteresis will occur, we find a very simple explanation of our hysteresis results. We must first emphasise that our hysteresis curves are all remarkable in that they are negative hystereses. The e.m.f. in an increasing positive or negative field is always greater than the e.m.f. in decreasing positive or negative field. And this is explained by the above hypothesis; for in a decreasing field the spontaneous magnetization of the cold end does not decrease as rapidly as the (greater) true magnetization at the hot end, and therefore the difference is less than for the increasing field. The abnormal hysteresis curves may thus be taken as a remarkably interesting proof of the spontaneous magnetization theory and of Gerlach's views in relation to it.

It is interesting to note that on plotting the square of the intensity of magnetization as a function of the field for the two temperatures, and then finding the difference curve between the two graphs, we obtain a hysteresis curve of quite a different form from that for the thermomagnetic e.m.f. This shows that the total magnetic energy is not the significant factor for the phenomenon. We can similarly satisfy ourselves that the induction in the wire is non-significant.

* *Z. f. Phys.* **62**, 253; **63**, 660 (1930).

† *Ann. d. Phys.* **14**, 3 (1932).

‡ *Ann. d. Phys.* **8**, 649 (1931).

We have noticed that a change in tension of the wire produces an e.m.f. even when the magnetic field is kept at zero, and that there is a hysteresis of this e.m.f. also. This is mentioned here only as further elucidation of the spontaneous-magnetization theory; more work is being done and results will be published later. Here we point out that tension will turn the magnetic vectors without changing their magnitude, and will not cause any reversal of their sense. This has been fully discussed by Gerlach and his collaborators* in connexion with the change of resistance produced by tension. It will thus be realized that the existence of hysteresis in the e.m.f. produced by tension is a satisfactory indication that the assumptions made above as regards hysteresis of the turning process are valid.

Phenomena at the Curie point. The Curie point for the wire used has not yet been determined with any great accuracy; but we have found that the thermomagnetic e.m.f. reaches saturation in a constant field when the temperature at the hot end is near 750°C . We may assume, in the light of Broili's† work, that the Curie point is close to this temperature. An estimate of the Curie-point temperature was also obtained from three separate cooling curves against a platinum-copper thermocouple. These all agreed in giving the temperature of recalescence as 735°C ., and the result is probably more accurate than that derived from the saturation temperature. But too much reliance cannot be placed on it; Gerlach has defined the Curie point in quite a different way‡, and his value may be different. In any case, however, we see that the curve for 710°C . shown in figure 2(b) corresponds to a temperature very near the Curie point at the hot end. This may account for the anomalous form, but no further explanation has as yet been found. We hope to investigate later.

Comparison with previous results. Broili, in the work already quoted, did not notice any hysteresis in iron below 500°C . The metal which he used was, however, much purer and softer than that used here; our material was a rather hard steel, and the occurrence of hysteresis may be more likely in it. It is interesting to note, on the other hand, that Broili found two distinct phenomena corresponding with the two different initial e.m.f. states mentioned in the present paper.

Generally Broili found curves which were very similar to the first quarter-cycles shown in figure 4. But if the iron was heated up to above 600°C . before the beginning of the cycle and allowed to cool, the cycles became like those in our figure 2(a). Broili interpreted this as due to some kind of "recrystallization" of the iron at temperatures above 600°C . But the curves shown in figure 2(a) were found by us in steel in which no recrystallization had taken place; the heating process was at no time given to the specimen. It therefore seems that a more careful investigation into the phenomenon is required before Broili's interpretation can be accepted.

It seems to us that incomplete demagnetization may account for the temporary negative e.m.f. obtained in the curves for small fields like that in figure 4. This would mean that Broili's results for his "non-recrystallized iron" are erroneous;

* See, e.g., Erno Englert, *Ann. d. Phys.* **14**, 589 (1932).

† *Ann. d. Phys.* **14**, 3 (1932).

‡ Gerlach and Schneiderhan, *Ann. d. Phys.* **6**, 772 (1932).

unless the fact that his is soft iron will account for the difference. At least we obtain curves with our hard steel which are similar to Broili's for the recrystallized iron; and probably the heating process of Broili does little more than destroy the magnetization left by the insufficient demagnetization process.

Broili describes the hysteresis of the e.m.f. in pure nickel wires, and we note that his curves are of the normal or positive form; the e.m.f. is greater in absolute value for decreasing positive or negative fields than for increasing fields. This results in a contradiction with the qualitative theory put forward to explain the negative hysteresis we found in steel. It is true that the e.m.f. in nickel is opposite in sense to that in iron, being directed from cold to hot temperatures; but nevertheless the absolute value of the e.m.f. should undergo the negative hysteresis in both metals.

In this connection we should like to point out that Broili appears to have neglected a probable source of error in his work. In the researches on nickel Broili used a copper-constantan thermocouple to control the hot temperature, and constantan usually contains about 40 per cent of nickel. The thermomagnetic e.m.f. developed in nickel is rather higher than that in iron, as his own work also showed. Now since a rapid temperature-drop exists in the constantan wire as it emerges from the heating oven in the field of the solenoid, one would expect a considerable e.m.f. introduced into the thermocouple circuit by the influence of the magnetic field.

Broili does not mention this, and apparently no tests were made to check it. It is possible therefore that there is in his results a spurious hysteresis error of the type discussed earlier in the present paper. It is proposed to go over the work with nickel wires in these laboratories, with this possible error in mind.

A NOTE ON INTERFERENCE TONES IN SUPERHETERODYNE RECEIVERS

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ABSTRACT. The question of interference tones, in the case of a superheterodyne receiver, presents certain features not encountered in the case of non-heterodyne types of receivers. Briefly, the problem involves (1) the reception of at least three signals, (2) double detection, and (3) a filter action between the two detectors. In the case of rectification by detectors with generalized characteristics, quantitative analysis is extremely complex. The form of the result, however, shows how large is the number of possible sources of interference tones. The specific case of square-law rectification is considered also.

WE shall consider a single-dial-control superheterodyne receiver in which the local-oscillator frequency is always greater than that of the desired signal. The voltage E at the grid of the first detector will be composed of three fundamentals, the desired signal voltage E_1 , the local-oscillator voltage E_2 , and E_3 due to the presence of an interfering signal. Then we may write

$$E = E_1 - E_2 - E_3 \quad \dots\dots(1),$$

$$e_1 \quad \text{where} \quad E_1 = e_1 \cos \omega t \quad \dots\dots(2),$$

$$e_2 \quad E_2 = e_2 \cos (\omega + n) t \quad \dots\dots(3),$$

$$e_3 \quad E_3 = e_3 \cos (\omega + f) t \quad \dots\dots(4),$$

f, n and where f may have any value, positive or negative, and n is supersonic and bears the same order of relation to ω as angular audio (modulation) frequencies bear to n . Tuning-circuit effects are assumed to be implicitly expressed by these values. Substituting equations (2), (3), and (4) in equation (1), and applying the well-known trigonometric transformations, we have

$$E = V \cos (\omega t + \phi) \quad \dots\dots(5),$$

$$V \quad \text{where} \quad V^2 = e_1^2 + e_2^2 + e_3^2 + 2e_1e_2 \cos nt \\ + 2e_1e_3 \cos ft + 2e_2e_3 \cos (n - f) t \quad \dots\dots(6),$$

$$\phi \quad \text{and} \quad \phi = \tan^{-1} \frac{e_2 \sin nt + e_3 \sin ft}{e_1 + e_2 \cos nt + e_3 \cos ft} \quad \dots\dots(7).$$

CASE 1. GENERAL RECTIFIER

We shall assume that the (current, voltage) characteristic of the first detector is of the form

$$i = a_0 + a_1 e + a_2 e^2 + \dots + a_r e^r + \dots \quad \text{.....(8),} \quad a_r$$

where i is the output current, e the input voltage, and the a 's are constants. The output current for an input voltage represented by equation (5) is then i, e

$$i = a_0 + a_1 V \cos(\omega t + \phi) + a_2 [V \cos(\omega t + \phi)]^2 + \dots + a_r [V \cos(\omega t + \phi)]^r + \dots \text{.....(9).}$$

Now the output circuit of this valve contains selective devices (usually band-pass filters) tuned to select, from the output current, only those components of angular frequency between $n + \epsilon$ and $n - \epsilon$, where ϵ is an angular audio frequency and ϵ/π is the width of the tuning curves of the selective devices. Rewriting equation (9) and expanding the powers of the cosines in terms of multiple angles we have ϵ

$$\begin{aligned} i = & a_0 + a_1 V \cos(\omega t + \phi) \\ & \frac{1}{2} a_2 V^2 + \frac{1}{2} a_2 V^2 \cos 2(\omega t + \phi) \\ & + \frac{3}{4} a_3 V^3 \cos(\omega t + \phi) + \frac{1}{4} a_3 V^3 \cos 3(\omega t + \phi) \\ & \frac{3}{8} a_4 V^4 + \frac{1}{2} a_4 V^4 \cos 2(\omega t + \phi) + \text{etc.} \\ & \dots \qquad \dots \qquad \dots \qquad \dots \end{aligned}$$

$$\begin{aligned} & \frac{r(r-1) \dots (r/2-1)}{2^r \cdot r/2!} a_r V^r + \text{terms in } \cos 2(\omega t + \phi), \cos 4(\omega t + \phi), \text{ etc.} \\ & + \text{terms in } \cos(\omega t + \phi), \cos 3(\omega t + \phi), \text{ etc.} \quad \text{.....(9a).} \end{aligned}$$

Here r is even only.

Only terms from the first column of equation (9a) will be selected by the selective devices. All other terms have angular frequencies of the order of ω and multiples of ω , and will not be taken into account in the present treatment. Considering only terms in the first column, we have

$$I = A_2 V^2 + A_4 V^4 + A_6 V^6 + \dots + A_s V^s + \dots \quad \text{.....(10),} \quad I, A_s$$

where s is even and the A 's replace the coefficients in equation (9a). The constant term a_0 has been omitted, since it does not contribute to the useful output. As we shall now be concerned only with qualitative results we need not consider the values of the A s. Substituting equation (6) in (10), we have

$$\begin{aligned} I = & A_2 [e_1^2 + e_2^2 + e_3^2 + 2e_1 e_2 \cos nt + 2e_1 e_3 \cos ft + 2e_2 e_3 \cos(n-f)t] \\ & + A_4 [e_1^2 + e_2^2 + e_3^2 + 2e_1 e_2 \cos nt + 2e_1 e_3 \cos ft + 2e_2 e_3 \cos(n-f)t]^2 \\ & + \text{etc.} \quad \text{.....(11).} \end{aligned}$$

Expanding the general term in equation (11) by means of the multinomial expansion (see appendix) we see that equation (11) is composed of terms whose angular frequencies are exactly represented in the following two-dimensional array

$$\left. \begin{array}{cccc} -, & f, & 2f, & 3f, & \dots \\ n, & n \pm f, & n \pm 2f, & n \pm 3f, & \dots \\ -, & 2n \pm f, & 2n \pm 2f, & 2n \pm 3f, & \dots \\ -, & 3n \pm f, & 3n \pm 2f, & 3n \pm 3f, & \dots \\ -, & \dots & \dots & \dots & \\ -, & \dots & \dots & \dots & \end{array} \right\} \quad \text{.....(12).}$$

p, q
 η, ϵ

By giving f an appropriate value, namely that given by $pf = qn + \eta$ where p and q are integers, and $\eta < \epsilon$, the various terms in the array actually contributing to the output current may be picked out. Thus, in the case where $p = 1, q = 2$, we see that the following terms contribute towards the output: $(2n - f), (n - 2f), (3n - 2f), (5n - 2f), (5n - 3f), (7n - 3f)$, and so on.

ξ

The term of angular frequency n in equation (12), standing alone in the first column, is always present in the output, and is the term representing the output when $E_3 = 0$; that is to say, when no interfering signal is present. All the other terms in equation (12) contributing to the output, when a value is assigned to f , have angular frequencies of either $n + \xi$ or $n - \xi$, where

$$\xi = \alpha \cdot \eta \leq \epsilon \qquad \dots\dots(13).$$

α
 ϵ

and α is an integer.
Thus the voltage ϵ applied to the grid of the second detector, on the assumption that the intermediate frequency amplifier does not introduce frequency distortion between the limits $n + \epsilon$ and $n - \epsilon$, is of the form

$$\epsilon = P \cos nt + Q_1 \cos (n + \xi) t + Q_2 \cos (n - \xi) t \qquad \dots\dots(14),$$

Q_1, Q_2

where P depends on powers of e_1 and e_2 only, and Q_1 and Q_2 on powers of e_1, e_2 , and e_3 .

Assuming that the action of the second detector also is represented by the general relation of equation (8), substituting equation (14) in equation (8), and expanding the series so obtained in the same manner as previously, we see that the audio output contains a number of whistling tones, the angular frequencies of which are integral multiples of ξ . The relative amplitudes of these are as follows:

Angular frequency	ξ	2ξ	4ξ	$8\xi \dots$
Amplitude proportional to	$P(Q_1 + Q_2)$	$Q_1 Q_2$	$Q_1^2 Q_2^2$	$Q_1^4 Q_2^4 \dots$

These whistling tones are additional to the bands of interference tones due to the various combinations of the modulation frequencies of E_1 and E_3 . In actual practice, when interference is being experienced with a one-dial-control super-heterodyne receiver, the frequencies ω, f , of the wanted and unwanted signals remain constant, and n varies slightly owing to inaccuracies in the ganging between signal-input and oscillator circuits.

Δn

Suppose that an interfering signal is producing whistling tones in the output of a receiver, and that the receiver-tuning control is adjusted so that the signal-input circuit is tuned over a range equal to the band-width of the desired signal. Suppose also that the angular frequency of the oscillator changes by an amount Δn during this operation. Now in the relation

$$pf = qn + \eta,$$

$\eta \Delta$

the value assigned to f is independent of variation in n . When n varies by Δn , η also must vary by $\Delta \eta$ in order that this relation may be true, and we have

$$q \cdot \Delta n + \Delta \eta = 0 \qquad \dots\dots(15).$$

Hence ξ and the multiples of ξ vary by an amount given by

$\Delta \xi$

$$\alpha q \cdot \Delta n + \Delta \xi = 0 \qquad \dots\dots(16),$$

That is to say, the whistling tones vary slightly in pitch. The amount of variation depends, of course, mainly on the accuracy of the ganging of the input and oscillator circuits. As a typical case consider a receiver designed to cover the wave-lengths from 200 to 600 metres, that is to say, covering one hundred channels each of 10 kc./sec. width, so that rotation of the condenser scale through 0.01 of the total scale reading is sufficient to tune completely through a station. The sections of a good modern ganged condenser are generally matched to within $\frac{1}{2}$ per cent or $1 \mu\mu\text{F.}$, whichever is the less. Taking this figure, it is clear that $\Delta C/C$ is of the order of 10^{-4} , where ΔC is the misalignment error between two sections, introduced by rotation of the condenser through a small amount. The variation in ξ is given, as before, by

$$\alpha q \cdot \Delta n \pm \Delta \xi = 0,$$

where

$$\Delta n + \frac{1}{2} (\Delta C/C) n = 0.$$

At a wave-length of 500 metres $n = 12\pi \times 10^5$ radians per second, and we have

$$\pm \alpha q \frac{1}{2} \cdot 10^{-4} \cdot 12\pi \cdot 10^5 = \Delta \xi,$$

or

$$\pm 60\pi \alpha q = \Delta \xi.$$

Therefore, in this case, the fundamental whistling tone varies in pitch by an amount of $\pm 30\alpha q$, where α and q are integers. In practice the pitch is found to vary by amounts of the order of 300, giving a value of the order of 10 to the product αq .

The whistling tones occur at several places around the tuning scale in the majority of commercial models of superheterodyne receivers when they are operated in the vicinity of a broadcasting station, and the writer has yet to meet an instrument which does not suffer from this trouble in some degree. The actual magnitudes of the tones cannot be determined until the various coefficients in the first and second detector functions are known. It is clear, however, that the amplitude of the fundamental tone, of angular frequency ξ , is greater than the amplitudes of the overtones of ξ .

CASE 2. SQUARE-LAW RECTIFIER

Assuming that the first detector (current, voltage) characteristic is of the form $i = kV^2$, and putting $f = \pm n \pm \epsilon$, we find that the terms selected from its output current by the intermediate frequency selective circuits are as follows:

$$I = k_1 [2e_1 e_2 \cos nt + 2e_1 e_3 \cos (n \pm \epsilon)t] \quad \dots\dots(17). \quad I, k_1$$

If we put $f = 2n$, we have the simple case of second channel interference, and the amplitude of the second term in equation (17) becomes $2e_2 e_3$.

If no distortion occurs in the intermediate frequency amplifier, the voltage applied to the grid of the second detector will be proportional to I in equation (17), and if this also operates as a perfect square-law rectifier, the audio output terms will be given by

$$k_2 I_A = 2e_1^2 e_2^2 + 2e_1^2 e_3^2 + 4e_1^2 e_2 e_3 \cos \epsilon t \quad \dots\dots(18). \quad k_2, I_A$$

If E_1 and E_3 are both modulated, the first term in equation (18) contains the desired signal plus harmonic distortion products. The second term may be ignored

if e_3 is small, and this frequently obtains in practice. If not, it represents ten interference bands. The last term gives a pure whistling tone plus fourteen interference bands. As in the general case, the whistling tone is of variable pitch, the variation depending on the accuracy with which the frequency of the local oscillator keeps n radians per second ahead of the signal-frequency circuit. The mutual effect of the signals results in an *increase* in the modulation of the desired signal, for

$$k_2 \Delta I_A / \Delta e_1 = 4e_1 e_2^2 + 4e_1 e_3^2 + 8e_1 e_2 e_3 \cos \epsilon t \quad \dots\dots(19),$$

in the presence of e_3 , and

$$k_2 \Delta I_A / \Delta e_1 = 4e_1 e_2^2 \quad \dots\dots(20),$$

in the absence of e_3 .

x The ratio x of expressions (19) and (20), giving the increase in modulation due to the interfering signal, is given by

$$x = 1 + (e_3^2 + 2e_2 e_3 \cos \epsilon t) / e_2^2 \quad \dots\dots(21),$$

and if e_3 be small this becomes

$$x = 1 + 2(e_3/e_2) \cos \epsilon t \quad \dots\dots(22).$$

(When $f = 2n$ this value, e_3^2 being neglected, becomes

$$1 + 2(e_3/e_1) \cos \epsilon t).$$

In the absence of the desired signal the interfering signal does not contribute to the audio output. There is, of course, an infinity of values which may be accorded to f , and in cases where the interfering signal is due to a powerful local station—that is to say, where e_3^2 is not negligible—each different value of f results in a different audio output and, in general, a different value of x . It would serve no purpose to consider further cases here, but there are certain conclusions which may be drawn from the preceding analysis.

The fact that the number of interference bands in the audio output is greatly reduced when e_3^2 is negligible stresses the importance of careful screening in the pre-first-detector stages. Further, a receiver employing a well-screened stage of radio-frequency amplification is, for the same reason, to be preferred to a receiver in which the first stage is the first detector. The use of band-pass filters and of circuits of low decrement in the signal-input circuit also aids in this direction.

These points are referred to only briefly as it is realized that the principles of superheterodyne-receiver design are now fairly well established, and, further, it would be out of place to discuss them in this paper.

APPENDIX

T_s We have to expand the general term T_s , where $T_s = A_s V^s$, in equation (10), where V has the value given by equation (6) and s is even. Replacing $e_1^2 + e_2^2 + e_3^2$ by $2e^2$ in equation (6) and writing the value of V^2 in full, we have

$$T_s = 2^{\frac{1}{2}s} A_s [e^2 + e_1 e_2 \cos nt + e_1 e_3 \cos ft + e_2 e_3 \cos (n - f) t]^{\frac{1}{2}s}.$$

Since s is even, $\frac{1}{2}s$ is integral, and expanding T_s by the multinomial expansion we have

$$T_s = 2^{\frac{1}{2}s} A_s \sum_{H, J, K, L=0}^{\frac{1}{2}s} \beta a^H b^J c^K d^L, \quad H, J, K, L$$

where $\beta = {}_H C_{\frac{1}{2}s} \times {}_J C_{\frac{1}{2}s} \times {}_K C_{\frac{1}{2}s} \times {}_L C_{\frac{1}{2}s};$ β

$$a = e^2; \quad b = e_1 e_2 \cos nt; \quad c = e_1 e_3 \cos ft; \quad d = e_2 e_3 \cos (n - f) t; \quad a, b, c, d$$

and $H + J + K + L = \frac{1}{2}s.$

As we are only concerned with the angular frequencies present in ΣT_s , the values of the coefficients will be ignored. It is clear that T_s is composed of a sum of products of powers of cosines which can be expressed in terms of multiple angles. Replacing the powers of the cosines by the multiple angle series, we see that each term in the summation T_s is itself a summation, and we obtain

$$T_s = 2^{\frac{1}{2}s} A_s \sum_{H, J, K, L=0}^{\frac{1}{2}s} \beta a^H \sum_{j, k, l=0}^{J, K, L} \gamma \cos jnt \cdot \cos kft \cdot \cos l(n - f) t, \quad j, k, l$$

where γ depends on the values of j, k , and l . Rewriting this, we have γ

$$T_s = 2^{\frac{1}{2}s} A_s \sum_{H, J, K, L=0}^{\frac{1}{2}s} \beta a^H \sum_{j, k, l=0}^{J, K, L} \gamma' [\cos \{(j + l)n + (k - l)f\} t + 3 \text{ similar terms}],$$

where γ' takes account of the additional constants introduced by the re-arrangement. In equation (10) we have

$$I = \sum_{s=2}^{\infty} T_s (s \text{ even}),$$

whence

$$I = \sum_{s=2}^{\infty} 2^{\frac{1}{2}s} A_s \sum_{H, J, K, L=0}^{\frac{1}{2}s} \beta a^H \sum_{j, k, l=0}^{J, K, L} \gamma' [\cos \{(j + l)n + (k - l)f\} t + 3 \text{ similar terms}].$$

Giving the successive values to j, k, l, H, J, K, L and to s we see that the angular frequencies of the terms in the summation are exactly contained in the expression $\kappa n \pm \lambda f$, where κ and λ are positive integers. When $\kappa n \pm \lambda f = \pm n \pm \eta$, where $\eta \leq \epsilon$, a value can be assigned to f , and the terms actually contributing to the output can be picked out, as has been stated in the text. The only values of κ and λ which must be excluded are those given by $\kappa > 1, \lambda = 0$, and $\kappa = \lambda = 0$, and hence the array (12) is obtained.

λ, κ, η

DISCUSSION

Mr A. HALL. The author mentions only interference due to the presence of incoming stations, but, as has been pointed out by Mr Willans, there can be interference when only one station is being received, the worst offender being the second detector valve. Even the fifth and sixth harmonics of the intermediate frequency originating at the second detector valve can cause serious interference. In one commercial form of superheterodyne receiver I have found an interference which I would like the

author to consider. One station was being received, namely, an oscillating wave-meter, the strength of the signal entering the receiver was fairly considerable, and the amplification of the receiver was adjusted to be fairly large by suitable adjustment of grid bias. Then if the receiver was tuned accurately by the wave-meter no interference was received and any modulation could be freely heard. But when the receiver was tuned to a frequency a few thousand cycles higher a serious heterodyne note was heard. This took place over the whole of the wave-band range. If the author can explain this trouble I shall be very thankful.

AUTHOR'S reply. Although in my analysis I set out to consider interference from a source external to the receiver, certain other forms of interference, such as that due to the generation of harmonics by the local-oscillator valve, or to back-coupling between the second and the first detector valves, may be readily taken into account by assigning appropriate values to f . With regard to the problem stated by Mr Hall, the data given are not sufficient to permit of a definite solution. If we put $e_1 = 0$ and $f = -\Delta\omega$ ($\Delta\omega \leq \epsilon$) we see that the output from the second detector valve contains only the modulation (if any) of the wave-meter signal. It is clear, therefore, that the whistling tone experienced in this case is due to some cause other than that treated in the present paper.

REVIEWS OF BOOKS

Les Bandes Moléculaires dans les Spectres Stellaires, par P. SWINGS. Pp. 29.
(*Actualités Scientifiques et Industrielles*, No. 50. Paris: Hermann et C^{ie}, 1932.)
7 francs.

The appearance of this excellent monograph is particularly welcome on account of the difficulty, which many readers experience, in finding the rather widely scattered papers on this important branch of astrophysics. It is a clear, concise and critical survey, such as might be expected of an author who has made a special study of the subject at the Yerkes observatory after carrying out elsewhere some laboratory investigations of certain band-spectra. The bands which have been identified in stellar spectra are all due to neutral diatomic molecules and occur only in the cooler stars (types *F*, *G*, *K*, *M*, *S*, *R*, and *N*). Amongst these molecules the author includes H_2 without a query or a comment, although some astrophysicists of long experience doubt the reported identity with sun-spot lines of certain H_2 band lines. To the author's list of molecules it seems safe to add SiH , band lines of which have been identified in the sun-spot spectrum. The band head at $\lambda 4752$ which, together with the one at $\lambda 4744$ due to $C^{12}C^{13}$, accompanies the strong $C^{12}C^{12}$ Swan band head at $\lambda 4737$ in certain stars, is attributed on p. 15 to $C^{12}C^{14}$. It should, however, be mentioned that this interpretation of the band has been questioned by Menzel, who attributes it, apparently with greater justification, to $C^{13}C^{13}$, thus removing any evidence there was of a third carbon isotope C^{14} . The booklet closes with a very useful list of references to original papers. It is the second of this admirable series of monographs dealing with the study of molecular bands in spectra of celestial sources, a former one (No. 16, 1929) by F. Baldet having been devoted to comet spectra.

W. J.

Structures et Propriétés Optiques des Carbonates, par H. BRASSEUR. Pp. 29.
(*Actualités Scientifiques et Industrielles*, No. 51. Paris: Hermann et C^{ie}, 1932.)
7 francs.

This monograph deals chiefly with the refractive indices, birefringences and related properties of carbonates in the two crystalline forms, e.g. of $CaCO_3$ in the well-known forms calcite and aragonite. It also includes a brief account of the same optical properties of certain crystals in which the CO_3 group is replaced by one of the groups BO_3 , NO_3 , TiO_3 . The subject is founded upon some of the researches of W. L. Bragg and later investigations by others, including the author himself, who, as we learn from a preface by V. Henri, has worked upon this subject in W. L. Bragg's laboratory and elsewhere. The four diagrams would gain in usefulness if specific reference were made to them either in captions or in the text itself and if symbols were included in all instead of only one of them. So broad a title seems hardly suitable for a monograph which excludes such important optical properties of these crystals as their infra-red spectra, about which much valuable information has been won by Liebisch and Rubens, by C. Schaefer and his collaborators and by Rawlins, Taylor and Rideal. Within its set limits the booklet is interesting and valuable.

W. J.

Acoustics and Architecture, by PAUL E. SABINE. Pp. ix + 327. (McGraw-Hill Publishing Co., Ltd.) 21s. net.

The two introductory chapters of this book contain those notions concerning the nature and properties of sound necessary for the appreciation of its principal theme, and justify the author's departure from the more usual title of "Architectural Acoustics" by which works of similar scope are known. In these chapters, which also provide an historical background, the essential preliminaries are disposed of in a simple but businesslike manner and the reader is introduced to the subject of sustained sound in an enclosure by the consideration of stationary and semi-stationary waves in a tube. We note that the diagram illustrating the last named system has the unusual merit of being correctly described and drawn, and, passing to a description of Prof. Wallace Sabine's work on the intensity distribution in a room, we meet one of the characteristic features of the book—the prominence given by the author to the pioneer work of his kinsman and the researches with which he himself has been associated at the Riverbank Laboratories. A description of W. C. Sabine's work may appeal especially to those without easy access to the *Collected Papers*, while an account of the author's work under a single cover and fitting easily into the general ensemble is too welcome to require the apology made in the preface. Reverberation is studied with absorption considered as a continuous and then, in the modern mode, as a discontinuous phenomenon, while the proofs of the corresponding reverberation formulae are based on Buckingham's analysis the kernel of which is given in an appendix. The methods of measuring absorption coefficients at normal and at random incidence having been described and the results considered, there follow two chapters of considerable practical interest. The first of these is concerned with the calculation of the reverberation time of an auditorium and a discussion of the "acceptable range of reverberation times," which expression the author prefers in place of "optimum reverberation time"; while, in the second, salient features of auditorium design are illustrated by architectural drawings of actual buildings. The account of the measurement and control of noise is good and on the subjects of sound-transmission and insulation the author has much to say that is of interest. Particularly valuable is his critical comparison of the methods that have been employed for measuring the transmission of sound by walls and his demonstration from the data obtained that, in general, it is the mass per unit area of the wall which plays the predominating rôle in sound-reduction. In the chapter devoted to machine isolation, oscillograms of machine and floor vibrations are reproduced and serve to illustrate the clear distinction which must be drawn between measures which reduce the vibration of the machine on its supports and those which reduce the transmission of vibration to the supporting structure. The book concludes with a number of appendices containing useful data on absorption coefficients.

This volume has been written by a master of the craft which it describes and, as it continuously reflects the eminently practical outlook of its author, it may be recommended not only to those whose interest is of an academic nature but also to those actively engaged in the design and acoustical correction of buildings.

E. J. I.

The Colloid Aspects of Textile Materials and Related Topics. A General Discussion held by the Faraday Society. London, 1933. Pp. 368. Price 15s. 6d. net.

By a striking coincidence this volume has appeared within a few weeks of the twentieth anniversary of the first general discussion on colloids arranged by the Faraday Society, that held on March 12, 1913, on the viscosity of colloids. Few things could more vividly impress a reader with the astonishing development of the discipline than a comparison of the two reports. Twenty years ago investigators were concerned much more in discovering strange and anomalous properties of colloidal solutions, and in developing a classification

and nomenclature, than in attempting to discover why a number of substances of the highest importance exhibited colloidal behaviour. It is on the latter problem that recent research on cellulose and proteins has concentrated, and it has achieved an astonishing measure of success by bringing into action the whole armoury of modern experimental methods. Measurements of the elastic and optical properties of natural and artificial cellulose fibres, X-ray analysis, viscosity measurements and determinations of the osmotic pressure of sols of cellulose esters, as well as the exhaustive application of classical chemical methods like methylation, have produced results which dovetail very satisfactorily. The structure of the cellulose fibre deduced from an imposing mass of concordant evidence is described as follows by Prof. H. Mark in his opening paper: "Cellulose...consists of fibres with a diameter between 1 and 5 deniers or 80 and 400 μ , which have often a very irregular shape. These fibres are built up from the so-called *cellulose micelles*. They are bundles of long molecular chains which are held closely together. We do not know exactly how many of these chains form one micelle, and it seems to depend to a very great extent upon the treatment which the sample has undergone, but we may estimate that one of these packets in native cotton or ramie fibres consists of about 40 or 60 of these chains. We have reason to believe that the single chains of one special sheaf are not all exactly of the same length and structure; it seems, however, that the differences are not very great, so that we are entitled to speak of a certain *average length* and structure of these chains. The diameter of a micelle is between 50 and 70 Å., so that one single fibre contains about ten million micelles in its cross section.

"The chains themselves are built up of glucose units linked together by consecutive 1-4-glucosidic bonds; they are called *main valence* chains and form the very backbone of the whole structure; their average length is not yet quite fixed but, it seems, one may assume for the most carefully treated natural samples that the chains contain about 150 or 200 glucose molecules, and that this number decreases very rapidly with every chemical treatment of the fibre. Glucose units, main valence chains and micelles are the three essential building stones of cellulose fibres."

The next problem of fundamental interest to the colloid physicists is: into what elements is this astonishing structure broken up when cellulose, or one of its esters, goes into solution? The answer "The micelle!" would have been unanimous a few years ago and would still be that given by a considerable number now, there being some diversity of opinion regarding the mechanism by which the high viscosity so characteristic of these sols was brought about. In recent years however Prof. Staudinger, who gives a comprehensive summary of his work, has been led to a different view, in the first instance by studying substances of high molecular weight which could be obtained in the laboratory by polymerization of comparatively simple bodies, e.g. polyoxymethylenes and polystyrenes. The chemical investigation of these bodies, and later of natural substances of high molecular weight like rubber and cellulose, "arrived at the result that these substances consist of very long molecules, in which a hundred or more single molecules are bound by means of main valencies into chains, and it was further proved that these molecules, which were termed fibre molecules (*Fadenmoleküle*), dissolve normally, like the molecules of substances of low molecular weight....The properties of their solutions can, therefore, not result from a micellar structure of the colloid particles and special solvation phenomena occurring with them, but the colloidal nature of the solutions is connected with the size and special shape of the molecules. The investigation of this connection and the results of viscosity experiments provided confirmation for the results found chemically."

A brief summary only of Prof. Staudinger's results can be given here. He calls *specific viscosity* the increase in viscosity produced by the dissolved substance, i.e. if η_r is the relative viscosity $\eta_{\text{solution}}/\eta_{\text{solvent}}$, then $\eta_{sp} = \eta_r - 1$. For long molecules he then finds

$$\eta_{sp}/c = K_m M,$$

where M is the molecule weight, K_m a constant for the particular homologous series, and c "the concentration of a primary molar solution," which quantity is defined as follows: "By the primary molecule of a long chain molecule is here designated that structural unit which, when regularly linked end to end, builds up the long chain molecule. The primary molecule of the normal paraffins and paraffin derivatives is the CH_2 group; a primary molar solution of such substances has, therefore, a concentration of 1.4 per cent." Since this quantity is also a constant for a given series, the formula states that, other things being equal, the specific viscosity is proportional to the molecular weight or the chain length. Prof. Staudinger assumes the molecules to be straight and to make "elastic oscillations like a glass fibre," but not to be flexible like say a silk filament. The effect of these oscillations is that the molecules have a "sphere of activity" which, *for purposes of calculation* (his italics), he takes to be a flat cylinder with the length of the chain as diameter and its diameter as height. Only solutions of such low concentration that the aggregate volume of these cylinders is smaller than the total volume of solution are suitable for the determination of molecular weights.

The somewhat arbitrary hydrodynamics does not seem to have troubled the meeting as much as the concept of straight molecules, which seems to have been unacceptable especially to the investigators of surface films, like Rideal, Adam and Katz. The question whether viscosity measurements can be utilized to determine molecular weights was, however, raised in a much more acute form by the results submitted by Prof. E. H. Buchner (with P. J. P. Samwel). The investigators had measured, by a new and ingenious method, what is undoubtedly the true osmotic pressure of cellulose acetate solutions in various solvents, and found mean values of 34,300 to 41,000 for different samples, which are in good agreement with those obtained by other methods. The specific viscosity of solutions of equal concentrations should therefore, according to Staudinger, be approximately the same, but actually it varies from 1.28 to 4.01. Incidentally the specific viscosity decreases rapidly with rising temperature which, needless to say, does not affect the molecular weight. The discussion did nothing to clear up this discrepancy. It may also be useful to point out that, in the absence of other evidence, osmotic-pressure measurements cannot distinguish between micelles and macromolecules; in fact, the emphatic distinction between the two may remind critical readers of a well-known epigram by Swift.

The fibres of animal origin, which consist of proteins, have been studied as far as their insolubility permits by the same methods as the cellulose fibres, and here again X-ray examination has confirmed and completed the picture first sketched by the chemist. Drs Dorothy Jordan Lloyd and Henry Phillips, acknowledging an earlier summary by Astbury, describe it as follows: "Silk, stretched hair or wool and collagen fibres have been shown to be built up of long chain molecules lying parallel to the fibre axis. The long molecules consist of a repeating unit, of which three atoms lie on the spiral or zig-zag axis of the molecule, while the remainder form lateral extensions—the whole being a long polypeptide chain with the length of the repeating unit 3.5 Å." How these structural units are combined in natural fibres, and how the mechanical properties depend on the configuration of these elements and on their grouping in the fibre, are questions which are dealt with in a number of fascinating papers. It is difficult to choose a single example, but perhaps the paper by Dr S. G. Barker on "The physical significance of crimp or waviness in the wool fibre" will serve as well as any to illustrate the intricacies of a single problem, and the great number of possible methods of attack from the physical side alone, which have to be supplemented by physiological and biochemical investigation on secretion and growth. Some of the relations found are surprisingly—and misleadingly—simple. Thus, if the true area of the cross section, which is elliptical, is taken into account, the product (area \times number of crimps per inch) is reasonably constant. In view of this result, research for some time was concerned chiefly with the number of waves per unit length of fibre, until further work showed that this figure was not really significant, but that "the total number

of crimps per fibre along its entire length" was constant for a given fleece. "In many locks the mean total number of crimps in each fibre was the same irrespective of the length of the fibre" although the difference between the length of the shortest and longest fibre amounted to as much as 9 cm.

The geometrical form of the crimp may be anything from a plane sine curve to a helix, with a number of intermediate types: thus the sine curve may not throughout its length lie in one plane, but in a succession of planes inclined to each other. Similarly the helix may have a pitch which varies or even changes sign, i.e. a right-handed helix may become left-handed and *vice versa*. A mathematical expression covering all these types has been formulated by Tunstall.

These regularities having been established by observation, there remains the formidable task of discovering the mechanism producing them. As with other structures of organic origin "models" can be produced by comparatively simple physical methods which can bear no real resemblance to what goes on in the organism: an oscillating jet of gelatin sol discharged into a dehydrating liquid sets to a filament which, after drying, closely resembles a wool fibre. Although surface tension effects and dehydration may be operative in the latter too, their action is spread over a very considerable period, and ancillary hypotheses postulating periodicity in the physiological activities of the secreting organ, the follicle, become necessary.

These, and much else contained in the volume under review, is outside the province of the physicist. But there is also much which will afford him the satisfaction of knowing that, in the comparatively short time during which the physicist has been called upon to assist in the study of textile fibres, he has certainly magnified his office.

E. H.

Lehrbuch der Glasbläserei, by CARL WOYTACEK. Technisch-Gewerbliche Bücher, Band 7. Pp. vii + 319. (Wien: Julius Springer.) Price RM. 22.50.

A good book on glass-blowing can be of great value to the research worker and laboratory assistant as well as to the professional glass-blower, and the above volume is one that can be recommended to all who are interested in the subject. The treatment is considerably more detailed and comprehensive than that found in the majority of books, and the portions dealing with glass-blowing proper are written with the clear style of the expert who knows precisely how to present his subject. The volume is divided into two sections, the first being a general introduction while in the second the manufacture of special apparatus is dealt with. At the beginning of part 1 a survey is made of the grades of glass in common use, and the selection of blowpipes, glass tools, blowers and similar apparatus. The author passes to the correct method of holding the glass tubing so that it can be rotated steadily in the flame. Instructions are given for drawing a capillary and a series of graded exercises lead to the more complicated work such as the manufacture of taps. This section of the book is admirable; every requisite detail is given and, when necessary, illustrated. The diagrams are a noteworthy feature; they are numerous and indicate clearly what is required at each stage of the work. The only limitation is that the book is written for continental workers and may require a little adaptation when applied to English conditions. There is, for example, no mention of pyrex glass and the type of flame best suited for working it. Probably the majority of readers would also have welcomed a chapter on the working of fused quartz in the blowpipe.

Instructions are given in the second section regarding the manufacture of all kinds of specialized apparatus—thermometers, barometers, standard volumetric and gas-analysis glassware, vacuum pumps, discharge tubes and mercury-vapour lamps. An immense amount of information is thus collected together, but it is doubtful whether all of it strictly belongs to a book on glass-blowing. For example, the description of Geryk, Gaede, and similar oil pumps could have been omitted and a reference to a suitable volume on vacuum

practice given. A difficulty that arises in some of the specialized branches is that, as the author admits, the assistance of an expert is required to obtain a working knowledge of the process. With such help detailed written instructions seem unnecessary, and without it they are not of very much use. On the other hand there are few who will not find much information that is useful in this section, and the book as a whole is the best work on glass-blowing that the reviewer has had the pleasure of reading.

K. H. P.

Heat, Light, and Sound, by E. NIGHTINGALE. Pp. xii + 378, with 11 plates and 363 figures. (London, G. Bell and Sons, Ltd., 1931.) 6s. 6d.

The writer of an elementary text-book of physics must necessarily travel a well-worn path. The author of this book, therefore, has contented himself with a ready-mapped route, and with few exceptions has followed the conventional order of treatment. None the less, new departures in two directions may be noted. Firstly a wider cultural value is given to formal observations and records, by the skilful insertion of historical accounts. In this way the beginner, for whom this book is written, is pleasantly introduced to the first principles and to their origins at the same time. Secondly, the text, broken up by many new and redrawn illustrations and diagrams, bears a fresh and interesting appearance. In a few places a certain laxity of description and explanation may be observed, as in the account of the joining of two ice blocks by pressure, p. 82; the statement that the blocks will stick together even under warm water hardly elucidates. The diffusion of air and hydrogen in wide jars does not immediately prove that "the molecules are in rapid motion" (p. 94). Such minor criticisms may be made, but these smaller faults do not obscure the outstanding attractiveness of the volume for both teacher and student, to whom it may be recommended with confidence.

J. P. A.

Experimental Hydrostatics and Mechanics, by E. NIGHTINGALE. Pp. x + 244, with 20 illustrations and 182 text figures. (London, G. Bell and Sons, Ltd., 1931.) 4s. 6d.

In this little book the methods successfully employed in *Heat, Light, and Sound* are developed in a more pronounced degree. Anyone whose youth was marred by the study of mechanics of the purely algebraic kind, with academic problems to be solved by formula at the end of each section, will desire to have this book, although it is meant for beginners. It is true that if in a critical mood he will find rather trying the frequently repeated qualifications "great," "remarkable," "famous," as applied to well-known investigators and experiments, but he is not a schoolboy. The historical developments are carefully described with new and interesting illustrations. After a general historical introduction, the book sets off with the principle of moments, centres of gravity, and equilibrium, employing a rough and ready definition of force. Hydrostatics follows. Then, after a more detailed study of force and equilibrium and the conceptions of work and power, dynamics and the laws of motion finish the book. This order, to which grave objection might be raised on logical grounds, is deliberately chosen as more suited to the beginner. While one may doubt the wisdom of this decision, there is no question that the author has revitalized the presentation of elementary mechanics. No teacher of the subject would be wise to neglect this book.

J. P. A.

Elementary Hyperbolics, by M. E. J. GHEURY DE BRAY. Vol. 1, pp. xi + 351. Vol. 2, pp. xii + 209. (London: Crosby, Lockwood and Son, 1931.)

The book is specially adapted to the requirements of beginners and is intended for those technical students who do not take easily to mathematics. Provided they are sufficiently tenacious of purpose such students will find every step filled in, so that they can

hardly be "stumped" in reading the book, though they will need all their wits about them if they are to retain the thread of an argument which extends over perhaps three pages of algebra.

If they are the sort of people who are helped by speaking of: "How we descend a flight of steps, and where they lead us" instead of "How to evaluate a continued fraction," then this book will certainly help them.

The reviewer feels that much of the difficulty of the hyperbolic functions would be removed if the hyperbola were not introduced. The difficulty as to the unit of measurement for the argument could not then arise, and much tedious algebra would be avoided.

What will be the reaction of the technical student to the assertion on p. 108 that if $2u = 2\theta$, then u is not equal to θ , we do not know. His shock will be no less severe than that of the mathematician who on another page is supposed to be horrified at the suggestion that $\cosh(\text{dog}) = \frac{1}{2}(e^{\text{dog}} + e^{-\text{dog}})$. Actually his surprise might be so small that he would even be prepared to admit that $\cosh x = \frac{1}{2}(e^x + e^{-x})$ even when $x =$ (the numerical value of) Gheury de Bray!

The second volume is devoted to the application of vectors and of hyperbolic functions to the solution of mechanical and electrical problems, and can be particularly warmly commended.

J. H. A.

Tables for the Development of the Disturbing Function with Schedules for Harmonic Analysis, by ERNEST W. BROWN and DICK BROUWER. Pp. 85. (Cambridge: University Press, 1933.) 10s. 6d.

The disturbing function R is such that dR/ds gives the disturbing force on one planet, in the direction s , due to another planet. When there are several disturbing bodies, R is the sum of a number of functions each of the form $m/\rho - mr \cos \omega/r'^2$ where m is the mass of the disturbing body, ρ the distance between the two, r, r' the distances of the disturbed and disturbing bodies from the sun and ω the angle between r and r' .

The numerical treatment of the function is facilitated by the expansion of

$$(1 - 2\alpha \cos S + \alpha^2)^{-n}$$

in the form

$$(1 - \alpha^2)^{-n} (A_n + B_n' \alpha \cos S + B_n'' \alpha^2 \cos 2S + B_n''' \alpha^3 \cos 3S + \dots),$$

the coefficients A and the first eleven of the coefficients B being given in this table for values $-\frac{1}{2}, -\frac{3}{2}, -\frac{5}{2}$ and $-\frac{7}{2}$ of $-n$. Actually the quantities tabulated are the logarithms to 7 figures of A and B for values of $\alpha^2/(1 - \alpha^2)$ from 0 to 2.50, proceeding by steps of 0.01. Natural values would be less useful even when a calculating machine is available, since products of several factors would normally be required.

We may note that the extraction of the factor $(1 - \alpha^2)^{-n}$ simplifies the numerical work but not the analytic nature of the B s which are quite closely related to ordinary Legendre functions if the expansion is made simply in powers of α .

The rest of the book contains other tables of use in precise calculation of orbits, the only other one likely to be of interest to the general physicist being the expansion of $(1 - 2\alpha \cos S + \alpha^2)^{-n}$ in the form $(1 - \alpha^2)^{-n-\frac{1}{2}}(C + D_n' \cos S + D_n'' \cos 2S + \dots)$ for $n = +\frac{1}{2}$ and $+\frac{3}{2}$. This time, the natural values to 5 figures are entered as functions of α itself, which proceeds from 0.900 to 0.950 by steps of 0.001.

The book is stated to be the same as part 5 of volume 6 of the *Transactions of Yale University Observatory*, and it has apparently been printed from the same plates, since the page numbers commence at 73.

J. H. A.

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JUNE, 1933

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